they must differ in chemical intensity. But what is chemical action? According to one view, it is a change in which chemical intensities are equalized, with a conversion of part of the chemical energies concerned into other energy forms; according to the other it is a union of atoms. But how can two things, which we suppose to be exactly alike, unite? Whence comes the difference of intensity? By virtue of what principle is the elementary diatomic molecule formed? If this molecule always preserved its integrity, we could regard its diatomic constitution as an elementary condition, but according to our chemical theories, the molecule in many chemical reactions is subject to division. Nevertheless, whenever the atoms are set free they combine according to the diatomic pattern.

It is thus roughly shown that the later views of chemical energy are not supported by the molecular hypothesis. Which shall we throw overboard for the sake of the other, or may we hope for a view which will embrace, possibly revise, and reconcile both?

THE TUNGSTATES AND MOLYBDATES OF THE RARE EARTHS.[1]

BY FANNY R. M. HITCHCOCK.

Received March 2, 1895.

THE estimation of molybdic and tungstic acids, and their separation from each other have been the subject of many investigations, but notwithstanding the time and care expended the results so far attained are not perfectly satisfactory, particularly as regards their separation. The reactions which take place when either element is tested alone cannot be depended upon when the two are together, each seeming to exert some modifying action on the other.

Several years ago, Smith and Bradbury[2] carried out a series of experiments on the precipitation of these two acids, chiefly with salts of the heavy metals. Their research brought out many new and interesting facts relating to the precipitation and

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[1] From the author's thesis presented to the Faculty of Philosophy of the University of Penn'a for the degree of Doctor of Philosophy, *1894*.

[2] *J. Anal. Appl. Chem.*, September, *1891*.

estimation of each acid separately, but failed to produce anything new in the way of a separation. It was with the hope that, by extending the investigation begun by them, to the action of other precipitants on these acids, additional information might be gathered which would lead to more definite results, that the experiments were undertaken, the results of which are offered in the following pages.

The molybdate solutions used in the work were made up from the sodium molybate. Analysis showed the salt to be pure and to agree with the formula given, $Na_2MoO_4 + 2H_2O$.

The tungstate solutions were prepared from the corresponding tungsten salt, $Na_2WoO_4 + 2H_2O$. Analysis showed that traces of silica and ferric iron were present, and molybdenum trioxide was found to the amount of three and one-tenth per cent. This was separated by Pechard's method.[1]

Due allowance has been made in all calculations for the amount of molybdic acid found in the sodium tungstate.

It was found best not to prepare more than 250 cc. of the solution of sodium tungstate at one time, as on standing it gradually affects the flask, the glass being attacked, and a sediment appearing which resembles silica, and is of noticeable amount. The solution of sodium molybdate also attacked the glass, but not so strongly nor so quickly as the sodium tungstate.

SODIUM TUNGSTATE AND MANGANESE SULPHATE.

The solution of manganese sulphate used was a saturated one. The solution of sodium tungstate contained 27.8600 grams to the liter, and, if completely precipitated by the manganese sulphate, ten cc. of the solution should yield 0.2871 gram of manganese tungstate, $MnWO_4$.

The precipitates all showed the same character, however varied the conditions under which they were formed, being flocculent at first and becoming slimy on standing. They filtered very slowly and were difficult to wash.

The filtrations were made through asbestos in a Gooch crucible, and the filtrates were all tested for tungstic acid by hydrogen sulphide in ammoniacal solution, the solution being subsequently acidified with hydrochloric acid.

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[1] *Compt rend.* 114, 173; *Ztschr.* Anorg. Chem., 1, 262; this JOURNAL, 15, 1, (*1893*).

A. Experiment 1.—Ten cc. of the sodium tungstate solution were diluted to 250 cc. with distilled water, brought to boiling, and fifty cc. of the manganese sulphate solution added. A voluminous precipitate formed at once, which was allowed to settle, then filtered off, washed with boiling water, dried in an air-bath at 180° C., cooled in a desiccator for three hours, and weighed.

Wt. obtained.	Wt. calculated.	Difference.
0.2310 gram.	0.2871	—0.0561 gram.

The filtrate gave a precipitate of tungsten trisulphide.

Experiment 2.—Ten cc. of the sodium tungstate solution were treated as before, but the precipitate was allowed to stand for two days, then filtered cold, and washed with hot water.

Wt. obtained.	Calculated.	Difference.
0.2779 gram.	0.2872	—0.0092

The filtrate gave a precipitate of tungsten trisulphide.

Experiment 3.—Ten cc. sodium tungstate solution were treated as before; the precipitate allowed to stand for twelve hours, then filtered cold, and washed with cold water.

Wt. obtained.	Calculated.	Difference.
0.2667 gram.	0.2871	—0.0204

Experiment 4.—Ten cc. sodium tungstate solution were treated as before; the precipitate was allowed to stand for twelve hours, then brought to boiling, filtered hot, and washed with a hot solution of ammonium nitrate.

Wt. obtained.	Calculated.	Difference.
0.2110 gram.	0.2871	—0.0693.

B. Experiment 1.—Ten cc. sodium tungstate solution were diluted to 250 cc. with distilled water, and five grams of ammonium nitrate added; the whole was then brought to boiling, and fifty cc. of the manganese sulphate solution were added; the precipitate was allowed to subside, filtered off, and washed with water containing ammonium nitrate; the filtrate was perfectly clear.

Wt. obtained.	Calculated.	Difference.
0.2351 gram.	0.2871	—0.0520

Experiment 2.—Ten cc. sodium tungstate solution were treated as in *B 1.* The precipitate was allowed to stand over night

before filtering, was filtered cold, and washed with cold water containing ammonium nitrate.

Wt. obtained.	Calculated.	Difference.
0.2393 gram.	0.2871	—0.0478

Both filtrates gave tungsten trisulphide.

C. Experiment 1.—Ten cc. sodium tungstate solution were diluted to 250 cc. with distilled water, and eighty cc. of ninety-five per cent. alcohol were added ; then fifty cc. manganese sulphate solution. The solution was heated, and the precipitate formed slowly. It was voluminous, white and flocculent, becoming granular on standing ; it was filtered off while still hot, washed with thirty-three per cent. alcohol, and ignited at a low temperature.

Wt. obtained.	Calculated.	Difference.
0.2666 gram.	0.2871	—0.0164

Experiment 2.—Ten cc. sodium tungstate solution were treated as in *C 1.* The precipitate was allowed to stand for several days before filtering, was filtered cold, and washed with thirty-three per cent. alcohol as before.

Wt. obtained.	Calculated.	Difference.
0.2707 gram.	0.2871	—0.0205

A brief inspection of the analytical results given in detail above shows beyond reasonable doubt that the precipitation of tungstic acid from its salts cannot be well hoped for when manganese salts are used as the precipitants. The most varying conditions failing to give any promise of even approximate success, further experiments with manganese salts were abandoned, and attention was turned to uranium salts. Trials were made with uranium acetate, uranyl nitrate, and uranyl chloride. With uranium acetate no precipitate formed in an aqueous solution of sodium tungstate, whether cold or hot, and an excess of either the tungstate or the acetate produced no effect. The addition of a few drops of acetic acid caused no change. Alcohol produced a slight opalescence, but though the solution stood for several days no precipitate formed. When uranyl nitrate was used a precipitate formed at once, which was pale yellow in color, flocculent, and quick to subside. The precipitation seemed to take place equally well in the presence of alcohol, and in that of ammonium salts.

The solution of sodium tungstate used contained five grams in a liter, and ten·cc. would therefore yield 0.0883+ gram of uranyl tungstate, if completely precipitated. The atomic mass of uranium was taken as 239.6.

A. Twenty cc. sodium tungstate solution were diluted with twenty cc. of distilled water and five cc. of a solution of uranyl nitrate added, the latter being in slight excess. This was followed by twenty-five cc. of a saturated solution of ammonium chloride, and the whole heated nearly to boiling for two hours, after which the precipitate was filtered off and washed first with water containing ammonium chloride, then with pure water. The filtration was made through Schleicher & Schull's 590 filter-paper, and the precipitate was ignited strongly with free access of air.

Wt. obtained.	Calculated.	Difference.
0.1728 gram.	0.1767	0.0039

The filtrate gave no trace of tungsten trisulphide when tested with hydrogen sulphide, and from the appearance of the precipitate after ignition some reduction had evidently taken place.

B. Twenty cc. sodium tungstate solution diluted with twenty-five cc. distilled water, were precipitated with five cc. of the uranyl nitrate solution. The precipitate was allowed to stand for one hour, was then filtered in the cold, and washed with cold water, on a tared filter which had been dried at 150° C. The precipitate was dried at the same temperature in an air-bath for two hours, and weighed at constant weight.

Wt. obtained.	Calculated.	Difference.
0.1770 gram.	0.1767	+0.0003

The filtrate, when tested, gave no trace of tungsten trisulphide. It may be added that when the ammonium chloride used in the first experiment was replaced by alcohol, the precipitation seemed to be equally complete, as there was no evidence of the presence of tungsten when the filtrate was tested with hydrogen sulphide.

To ascertain whether the tungstic acid could be determined volumetrically, the following experiment was made:

A solution was prepared containing fourteen grams of uranyl nitrate in one liter of water. Twenty cc. sodium tungstate solution were diluted with twenty-five cc. distilled water, and the nitrate solution introduced from a burette, the tungstate solution being constantly stirred, and the end-reaction ascertained by testing with potassium ferrocyanide on a porcelain plate.

Toward the last the reaction is rather slow, so that a brown color may be obtained with the potassium ferrocyanide before the tungsten is fully precipitated. If, however, the solution be allowed to stand a few seconds after each addition of the uranyl nitrate solution, no coloration is obtained on testing, unless the reaction is complete. By a little care the end-reaction can be made extremely close. Upon substituting a solution of uranyl chloride for the nitrate, equally good results were obtained.

SODIUM MOLYBDATE AND URANIUM SALTS.

A solution was prepared containing 8.51 grams of sodium molybdate to the liter, and the same salts of uranium were tried that had been used in the experiments with tungstic acid.

With uranium acetate, sodium molybdate behaved similarly to sodium tungstate, no precipitate being obtained by any method tried. With the nitrate of uranium, however, a precipitate is formed at once which redissolves on stirring, though not completely, a small quantity of some flocculent material remaining undissolved ; boiling did not bring down any further precipitate, and an excess of the nitrate had no effect. The uranyl nitrate solution was the same as that used with sodium tungstate, and contained fourteen grams to the liter. On trying a concentrated solution of uranyl nitrate a dense precipitate formed at once, which, on dilution, dissolved in part, but very imperfectly.

Addition of alcohol does not change the behavior in either a cold or a hot solution.

A solution containing twenty-five cc. of a saturated solution of ammonium chloride, twenty cc. of the sodium molybdate solution, and twenty-five cc. of water gave no permanent precipitate with uranyl nitrate, but when twenty cc. of the sodium molybdate solution were diluted with twenty-five cc. water, and the uranyl nitrate solution added in excess, the addition of ammonium chloride brought down the whole of the molybdenum.

With uranyl chloride, a precipitate was obtained at once, which, like that produced by uranyl nitrate, redissolved on stirring, as fast as it formed.

On standing, a pale lemon yellow precipitate appeared, which on heating went into solution. With the addition of an excess of uranyl chloride to the cold solution, a precipitate forms similar in appearance to the one just described, but on heating it does not redissolve. Heated for an hour it grows denser, and gradually becomes crystalline. These crystals are insoluble in water, and those which I obtained were washed first by decantation, then on the filter with cold water, dried on the air-bath at 128° C. (without any alteration in appearance), and analyzed.

The molybdic acid was determined by heating the salt in a current of hydrogen chloride gas. The $MoO_3.2HCl$ came off readily at a low heat, the salt in the boat changing in color from a brilliant golden yellow to a light green, then to a golden brown, and finally to a dark green, almost to a black.

This blackish residue when treated with concentrated hydrochloric acid did not dissolve; with aqua regia it did slowly dissolve to a deep yellow solution from which the uranium was precipitated by ammonium hydroxide; the precipitate after strong ignition had a metallic appearance. It was dissolved in concentrated nitric acid, evaporated to dryness, and gradually heated to a dull red heat. The brownish yellow powder obtained was weighed as uranium trioxide.

A slight loss occurred when the salt was heated in the stream of hydrogen chloride gas. as a little was carried over mechanically, and heated so strongly to the walls of the tube that it could not be removed.

The weight of material taken for analysis was one-tenth of a gram. The weights obtained were as follows:

Molybdenum trioxide = 0.0333 gram = 33.3 per cent.
Uranium trioxide = 0.0620 gram = 62.0 per cent.

These values correspond very closely to the formula UrO_2MoO_4, when the radicle MoO_4 may be regarded as replacing the two chlorine atoms in the uranyl chloride. The theoretical amounts required for this formula are

Molybdenum trioxide = 0.0334 gram = 33.4 per cent.
Uranium trioxide = 0.0666 gram = 66.6 per cent.

Water of crystallization does not seem to be present; one-tenth of a gram of the substance was dried over sulphuric acid for two days, and then in the air-bath for two hours at a temperature of 128° C. The loss in weight was eight-tenths of a milligram. On strong ignition the color changed at first a light green, then to a golden brown, and on cooling became once more bright yellow. By this ignition a loss in weight occurred amounting to nine and three-tenths millligrams; a second ignition caused no further loss.

Both before and after ignition the salt is readily soluble in hydrochloric acid, apparently without decomposition, as no reaction for uranium is given by the solution when tested with potassium ferrocyanide.

The perfect precipitation of tungstic acid by uranyl nitrate from the sodium tungstate solution, and the non-precipitation of molybdic acid by the same reagent, encouraged a hope that a separation of the two acids might be possible through its means.

As potassium ferrocyanide indicated the end reaction so sharply between sodium tungstate and uranyl nitrate, some tests were made with it as an indicator, with solutions of sodium molybdate and uranyl nitrate. Observing the same precautions as before the end reaction was equally sharp. It was observed, however, that the red color imparted to the potassium ferrocyanide by a drop of the molybdate solution as soon as the uranyl nitrate was in excess, gradually disappeared. and was not restored by the further addition of uranyl salts. The conditions were next varied by introducing the potassium ferrocyanide into the molybdate solution instead of making the tests on a porcelain plate as heretofore. Twenty cc. of sodium molybdate were diluted with twenty-five cc. of water, and five cc. of potassium ferrocyanide added. The uranyl nitrate solution was then run in, the red color appearing when 33.3 cc. of the uranyl nitrate had been used; an excess of six or seven cc. were added, and a deep red solution formed, but no precipitate appeared. After standing for two hours the red color had disappeared, and the solution had become yellow. A portion of this was tested with potassium ferrocyanide, but no reaction was obtained for uranium.

The addition of uranyl nitrate to another portion showed no excess of the potassium ferrycyanide. On substituting uranyl chloride for the nitrate the red solution was not obtained, but a reddish brown precipitate came down which was much lighter in color than that given by the uranyl salts alone.

Twenty cc. sodium tungstate solution were mixed with five cc. of the sodium molybdate solution, and diluted with twenty-five cc. of water; the uranyl nitrate solution was next run in from a burette, and the end reaction ascertained by potassium ferrocyanide on a porcelain plate. After standing for an hour the precipitate was filtered off in the cold, and washed with thirty-three per cent. alcohol.

It was hoped that the filtrate would contain the molybdenum, but examination showed that the greater part of it had been precipitated with the tungsten.

A second solution was prepared and titrated in the same manner as before; the precipitate with the supernatant fluid was then heated for an hour at a temperature of 60° C., filtered while hot, and washed with hot water containing thirty-three per cent. of alcohol. The molybdic acid was found in both filtrate and precipitate, though more went into the filtrate than in the first case.

On substituting uranyl chloride for the nitrate and repeating the titration, only a slight precipitate of the tungsten formed, the greater part dissolving with the molybdate, as fast as formed.

An excess of uranyl chloride brought down both the tungsten and the molybdenum completely. It was evident that no separation could be hoped for by means of uranium salts. There seems to be a tendency on the part of the members of the chromium sub-group to form compounds with each other which are not readily broken up, and which probably contain complex radicles of as yet unknown constitution. This is very strongly indicated by the behaviour of molybdic acid with uranyl salts. and the failure of the resulting compound to react in solution, for uranium with potassium ferrocyanide.

As the chief object of my investigations was to ascertain the manner in which the rare earths would act with tungstates and molybdates, these were now taken up and studied in detail. As the quantity at my disposal of any one of the rare earths used was necessarily very limited the material had to be worked over frequently, and a great deal of time was in consequence consumed by this preparatory work.

SODIUM MOLYBDATE AND CERIUM SULPHATE.

The solution of sodium molybdate used contained 13.24 grams to the liter, so that ten cc. of the solution should give 0.1628 gram of cerium molybdate, $Ce_2(MoO_4)_3$ if fully precipitated. The solution of cerium sulphate used was saturated.

Experiment.—Five cc. of the sodium molybdate solution were diluted to 150 cc. with distilled water, and ten cc. of the cerium sulphate solution added in the cold. A voluminous, white gelatinous precipitate formed at once. This stood for eighteen hours, when it had become granular in appearance and was yellow in color. It was filtered cold, washed with cold water, ignited and weighed. The theoretical weights are all calculated for the formula $Ce_2(MoO_4)_3$.

Wt. obtained.	Calculated.	Difference.
0.0760 gram.	0.0814	—0.0054

Experiment 2.—Five cc. of the sodium molybdate solution diluted to 150 cc. with distilled water were brought to boiling, when ten cc. of the cerium sulphate solution were added. A white precipitate formed at once, soon becoming curdy, and then granular, the color changing to yellow. This was allowed to stand for twelve hours, was then filtered, and washed with hot water, ignited and weighed.

Wt. obtained.	Calculated.	Difference.
0.0752 gram.	0.0814	—0.0062

Experiment 3.—Ten cc. sodium molybdate solution were diluted to 500 cc. with distilled water, and fifteen cc. of the cerium sulphate solution added in the cold. The precipitate after standing for twelve hours was filtered on asbestos in a Gooch crucible, ignited and weighed.

Wt. obtained.	Calculated.	Difference.
0.1596 gram.	0.1629	—0.0033

Experiment 4.—This was a duplicate of No. 3, excepting that the filtration took place as soon as the precipitate had settled.

Wt. obtained.	Calculated.	Difference.
0.1555 gram.	0.1629	—0.0074

From both filtrates additional precipitates were obtained on boiling.

Experiments 5 and 6.—Ten cc. of the sodium molybdate solution were diluted to 110 cc. with distilled water and brought to boiling, when fifteen cc. of the cerium sulphate solution were added; after two hours the precipitate was filtered off, washed with hot water, ignited and weighed.

	Wt. obtained.	Calculated.	Difference.
5.	0.1496 gram.	0.1629	—0.0133
6.	0.1587 "	0.1629	—0.0042

Experiment 7.—Ten cc. sodium molybdate solution were diluted to 110 cc. with distilled water, fifteen cc. of cerium sulphate solution added in the cold, and the whole brought to boiling, when twenty-five cc. of ninety-five per cent. alcohol were added. The precipitate was filtered off through Schleicher and Schull's 590 filter-paper, washed with fifty per cent. alcohol, ignited and weighed.

Wt. obtained.	Calculated.	Difference.
0.1588 gram.	0.1629	—0.0041

Experiment 8.—Ten cc. of sodium molybdate solution were diluted to 110 cc., fifteen cc. of cerium sulphate solution added in the cold, the whole brought to boiling, when one-third the volume of ninety-five per cent. alcohol was added. The precipitate stood for twelve hours before filtering; it was apparently not homogeneous, as a fine white powder was mixed through the yellow cerium molybdate. The filtering was very slow, and the washing with fifty per cent. alcohol was continued for two days.

Wt. obtained.	Calculated.	Difference.
0.2118 gram.	0.1629	+0.0489

Experiment 9.—Ten cc. sodium molybdate solution were diluted to 100 cc. and fifteen cc. cerium sulphate solution added in the cold, followed by one-third the volume of ninety-five per cent. alcohol. The precipitate was filtered after standing for two hours, and like that in No. 8, was not homogeneous in appearance.

Wt. obtained.	Calculated.	Difference.
0.1919 gram.	0.1629	0.0290

Experiment 10.—Ten cc. of sodium molybdate solution were diluted to 100 cc., and fifteen cc. cerium sulphate solution added.

The whole was boiled for an hour, allowed to cool, when one-third the volume of ninety-five per cent. alcohol was added. After standing twelve hours, it was filtered, washed with fifty per cent. alcohol, ignited and weighed.

Wt. obtained.	Calculated.	Difference.
0.2156 gram.	0.1629	0.0497

The precipitates from 8, 9 and 10, after ignition, were dissolved in hydrochloric acid, and tested with barium chloride; all gave precipitates of barium sulphate, as was expected. The following experiments were then made to determine what proportion of alcohol could be added without causing the cerium sulphate to precipitate.

a. Five cc. of the cerium sulphate solution were diluted to sixty cc., then twenty cc. of ninety-five per cent. alcohol were added in the cold, and, no precipitate forming, more alcohol was added, five cc. at a time, until seventy cc. in all had been introduced. The solution still remained perfectly clear.

[TO BE CONTINUED.]

SOME NEW LABORATORY APPARATUS.

BY EWALD SAUER.

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I. HOT AIR MOTOR FOR LABORATORY PURPOSES.

IN laboratories mechanical power is desirable for many undertakings which require continued shaking and stirring of liquids, as well as for rotation and grinding. While the factory steam-engine furnishes usually the necessary power for the laboratory of the technical chemist, nevertheless it is often desirable to have a separate source of power in case, for instance, of this not being in use.

For this purpose the turbines constructed by Raabe[1] have proved themselves useful in certain kinds of work, but only when small power is required. For many purposes the power is too weak, *e. g.*, the shaking of large quantities of liquids and the stirring of thick liquids.

The hot air motor of Heinrici, which is pictured below, and which has already proved of practical value in several labora-

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[1] *Ber. d. chem. Ges.*, *1888*, p. 1200.