

This, and other suggested corrections were, however, never made in any subsequent edition of Simson's Data. There are, in fact, other errata and corrigenda mentioned in these letters which were not corrected in the subsequent editions; and Simson complains in strong language of the "stupid conduct of John Balfour" in getting the second 8vo edition printed in Edinburgh; and says that some of it is "so spoiled" as to be unintelligible. I have had no opportunity of collating the earlier editions since these letters were placed in my hands, and can hence offer no distinct opinion as to the corrections of the errors thus introduced. I have done, however, the next best thing,—communicated the errata noticed in these letters to the editor of the best edition of Euclid we possess, Mr. Potts of Cambridge; although from the evident care which that gentleman has bestowed upon his work, I think it likely that few, if any of them, will have previously escaped his scrutiny.

I propose in the next sections to give three original letters from John Bernoulli to Cramer. Their length, however, will preclude the possibility of the slightest comment.

Royal Military Academy, Woolwich,
November 8, 1848.

LXXVI. *On the Atomic Weight of Molybdenum and some of its Compounds.* By L. SVANBERG and H. STRUVE.

[Continued from p. 434.]

PART II.

Behaviour of Molybdic Acid towards Phosphoric Acid.

ALTHOUGH the behaviour of molybdic acid towards phosphoric acid was not intimately connected with the object of our investigation, yet we were so frequently led to it that we considered it necessary to make some experiments upon the subject. This behaviour is so peculiar and so complicated that it requires a far more minute examination than we were able to devote to it, but since we have noticed some phænomena which have not hitherto been described, we consider it important to communicate in this place all that we have observed. The curious behaviour of molybdic acid towards phosphoric acid has been briefly noticed by some chemists. Berzelius* says, "When moist molybdic acid is mixed with phosphoric acid, it instantly becomes of a lemon colour; heat then dissolves it. The filtered liquid is colourless, and on evaporation leaves a tenacious transparent mass, which exhibits not the least sign of crystallization, and possesses a

* *Lehrbuch der Chemie*, 1845, vol. iii. p. 1044.

very astringent taste. Both water and alcohol dissolve it readily, the latter with a yellow colour, which on evaporation changes to blue, and leaves a brown opaque residue, which dissolves in water with a blue colour. When an excess of molybdic acid is digested with phosphoric acid, the latter is precipitated and forms with the molybdic acid a lemon-coloured basic salt which is insoluble in water."

These observations are quoted by Gmelin*, who has added to them the following:—"When a very little phosphoric acid is added to a concentrated solution of the molybdate of ammonia, and then large quantities of muriatic, sulphuric, or nitric acid, or first one of these acids and then a little phosphoric acid, a lemon-coloured crystalline powder falls, the more quickly the more concentrated the liquid; this powder contains besides molybdic acid some ammonia, but none, or extremely little, phosphoric acid; it forms with potash a colourless solution with evolution of ammonia, from which it is again precipitated by muriatic acid by long boiling; but if the solution in potash is evaporated to dryness, and the residue dissolved in water, muriatic acid then merely gives it a yellow colour, but muriatic acid and chloride of ammonium precipitate a yellow powder. The yellow powder gives with hot sulphuric acid a colourless solution which is not precipitated by water. It is but very sparingly soluble in cold water, dilute sulphuric, hydrochloric, or nitric acid, it dissolves slightly in boiling water without colour."

When molybdic acid, obtained by calcining a pure molybdate of ammonia, is mixed with an excess of phosphoric acid, scarcely a trace is dissolved at the ordinary temperature; but on heating the mixture, a perfect and colourless solution soon results, which forms, when quickly evaporated, a colourless vitreous non-crystalline mass. But if some water is added to this, or it is allowed to absorb moisture from the air, it acquires a beautiful blue colour, which however again disappears on evaporation. If, on the contrary, an excess of molybdic acid is employed, and gradually some drops of phosphoric and nitric acid added to it (we employ nitric acid to be sure of having all the molybdenum as molybdic acid), on the application of heat the colour of the molybdic acid first becomes lemon-yellow, then gradually the solution acquires also a yellow colour; a portion of the molybdic acid remains unaltered, whilst another portion is converted into a yellow powder. When nothing further is dissolved the solution is filtered; on evaporating it to dryness to expel the nitric acid, a yellowish-white amorphous mass is obtained, which dissolves in water, and also

* *Handbuch der Chemie*, 1844, vol. ii. p. 501, 511.

in weak and in strong alcohol, with a yellow colour. But if the dry mass is heated for some time, it gradually assumes a dark yellow colour, but still continues soluble in water. On treating molybdic acid with a little phosphoric acid, a portion separated as a yellow insoluble powder; more of this is formed every time the solution is evaporated, whether the evaporation be carried on in the water-bath or on the sand-bath. If the dry mass be heated somewhat more strongly in a platinum crucible, it turns green, and on increasing the temperature, fuses to a liquid which solidifies on cooling into a vitreous dark blue or dark green mass. If the temperature be raised so high that the crucible is incandescent, some molybdic acid is volatilized. This coloured mass dissolves with difficulty in cold water; with boiling water it forms a coloured solution, which, when evaporated with access of air, first becomes colourless and then reacquires the yellow colour. This colour may be instantly produced by the addition of a few drops of nitric acid.

This more or less yellow compound of phosphoric and molybdic acid dissolves readily in ammonia, forming a colourless liquid. But if to the concentrated solution either sulphuric, muriatic, or nitric acid is added (the last is best), a lemon-coloured precipitate is formed as soon as the liquid has an acid reaction. In this case, therefore, none of the phenomena previously described as occurring in the treatment of pure molybdic acid and ammonia take place; there acid salts, partly crystalline, partly amorphous, separated with a white colour whatever acid was used, whilst here, however great an excess of acid is employed, the yellow precipitate only is obtained. Moreover all the compounds of molybdic acid with the alkalies are very readily soluble in an excess of muriatic acid, whilst this yellow precipitate is insoluble.

When this yellow precipitate is collected upon a filter, the mother-liquor passes through with a yellow colour, and furnishes on evaporation more of the yellow salt, so that at last the liquid becomes perfectly colourless. On washing with pure water, the precipitate goes through the filter, which may however be prevented by the addition of a few drops of nitric acid. The colourless mother-liquor, which contains a large excess of nitric acid, furnishes on evaporation a colourless vitreous mass, from which ammonia and nitric acid precipitate no more yellow salt; but this residue nevertheless contains molybdic and phosphoric acid, and is acted upon by heat in the same manner as the yellow salt; however, the amount of the precipitate is far greater; but further experiments must show how this different behaviour is to be explained. Perhaps the state of the phosphoric acid in these compounds acts a very import-

ant part accordingly as we have to do with *a*-, *b*-, or *c*-phosphoric acid.

We adopted this method for the preparation of the insoluble yellow compound in order to be perfectly certain of obtaining a pure preparation; however, as the following analyses will show, the salt can be prepared more quickly in a much more simple manner. Molybdic acid is dissolved in an excess of ammonia and a few drops of a solution of phosphate of soda added, the liquid heated and mixed with an excess of one of the above-mentioned acids, when the yellow salt is instantly precipitated. To ascertain the composition of this salt we made the following analyses:—

I. 1·2258 grm. salt, prepared according to the first method, and dried at 212°, gave on calcination, with the addition of a few drops of nitric acid, 1·1095 molybdic and phosphoric acid. This residue was dissolved in ammonia, the molybdenum precipitated as sulphuret, and the phosphoric acid determined in the filtered solution, after it had been somewhat evaporated and mixed with chloride of ammonium, by magnesia. The weight of the ignited phosphate of magnesia amounted to 0·0699 = 0·0445 phosphoric acid. 100 parts of the salt consequently contained—

Oxide of ammonium + water	9·488
Phosphoric acid	3·631
Molybdic acid	86·881

II. 4·7247 grms. salt, prepared according to the second method, and dried at 212°, lost on ignition 0·478 grm. oxide of ammonium and water; the phosphoric acid was not determined. 100 parts contain—

Oxide of ammonium + water	10·117
Molybdic and phosphoric acids	89·833

In this analysis the loss on ignition is too high owing to the difficulty of oxidizing the residual mass, which consisted partly of oxide of molybdenum.

It seems to follow from analysis I. that the phosphoric acid in this salt is not an essential constituent according to the ordinary laws of chemical combination, and if it be neglected, the two analyses agree tolerably well with the theoretical composition of a pentamolybdate of ammonia, which contains—

	<i>a.</i>	Calc.	<i>b.</i>	Calc.
1 at. Oxide of ammonium	324·980	6·656	324·980	6·747
1 at. Water	112·479	2·304	112·479	2·335
5 at. Molybdic acid	4444·830	91·040	4379·145	90·918
	4882·289	100·009	4816·604	100·000

This salt, which is insoluble in water and acids, appears amorphous even under a high magnifying power, and to consist of minute spheres. When treated with potash, ammonia is expelled and a colourless solution obtained. When this salt is heated for some time in a closed platinum crucible, at a temperature below red heat, the whole of the ammonia and water escape, and a confused mass remains, which is partly of a brown, partly of a green colour. On treating this residue with concentrated nitric acid, very little reaction occurs at the ordinary temperature, but on heating it, nitrous acid is given off; the reaction, however, lasts only for a few moments; the liquid has now a beautiful yellow colour, and the sediment, a grayish-blue powder, is not further acted upon by nitric acid. The insoluble residue behaves like molybdic acid, dissolves in potash and in ammonia, and upon the addition of an acid, again furnishes the yellow salt. But the yellow solution possesses totally different properties. If this solution is dilute it loses the yellow colour in the cold and becomes colourless, but when heated it again makes its appearance. If this solution, which contains a large excess of nitric acid, is evaporated, some crystals separate on cooling, which appear under the microscope to be minute rhombohedrons. But this compound is not very stable, the mass absorbs water, all the crystals dissolve, and now another compound separates in regular octahedrons. Both these salts are very readily soluble, owing to which we were unfortunately unable to obtain a sufficient quantity of a pure salt for analysis.

If this yellow liquid be further evaporated, the yellow crystalline salt gradually passes into the amorphous yellow compound above described. If the yellow ammonia salt is heated with an excess of potash until the liquid no longer smells of ammonia and is partly evaporated, a colourless solution is obtained. On adding nitric acid to it, a yellow crystalline precipitate falls, which is insoluble in an excess of acid; it is collected and washed in the same manner as the preceding ammonia salt. It crystallizes in minute four-sided prisms, is insoluble in water, parts with water at a red heat, melts and solidifies into a crystalline yellow mass on cooling.

Analysis.—1·472 grm. salt lost on ignition 0·072 water, and gave 0·306 sulphate of potash = 0·1654 potash. But the sulphate of potash contained traces of phosphate of potash. The per-centage composition of the salt dried at 212° is accordingly—

Potash . . .	11·234
Molybdic acid	83·875
Water . . .	4·891

The anhydrous salt contains—

Potash . . . 11·812

Molybdic acid 88·188

In this analysis the molybdic acid was estimated from the loss. These results correspond with the pentamolybdate of potash previously described, with this difference, that the salt dried at 212° contains 4·891 water of crystallization, corresponding to 2 atoms. The theoretical composition of the salt is—

	a.	Calc.	b.	Calc.
1 at. Potash . . .	588·856	11·198	588·856	11·339
5 at. Molybdic acid	4444·830	84·524	4379·145	84·329
2 at. Water . . .	224·958	4·278	224·958	4·332
	5258·644	100·000	5192·959	100·000

If the yellow salt of ammonia is dissolved in ammonia and chloride of barium added, a white precipitate is formed, which possesses all the properties of the neutral molybdate of baryta described in the first part of this paper, with this sole difference, that when an acid is added to it, it instantly assumes a yellow colour. We have made two analyses of this salt, prepared at different times.

I. 0·780 grm. salt lost 0·0143 grm. on ignition, and gave 0·5994 sulphate of baryta = 0·3905 baryta.

II. This salt was analysed according to the following method, as we wished to determine the amount of phosphoric acid. After the loss had been determined by heating to redness, the powder was mixed in a beaker with a solution of sulphate of ammonia and hydrosulphate of ammonia. In this manner the whole of the molybdenum and phosphoric acid were obtained in solution of a dark brown colour, and the sulphate of baryta could be collected on a filter and easily washed. The filtered solution was mixed with muriatic acid, the sulphuret of molybdenum collected on a filter, and the liquid evaporated: this contained the phosphoric acid; it was first mixed with an excess of ammonia and then with sulphate of magnesia, and the precipitated phosphate of magnesia collected upon a filter after having stood for 24 hours, washed with water containing ammonia, dried, ignited and weighed. 0·937 grm. salt lost on ignition 0·015, and gave 0·7279 sulphate of baryta = 0·4736 baryta and 0·016 phosphate of magnesia = 0·0102 phosphoric acid.

The salt dried at 212° consequently contains in 100 parts—

	I.	II.
Baryta	50·074	50·543
Oxide of ammonium . .	1·833	1·601
Molybdic acid } . .	48·093	46·769
Phosphoric acid }		1·087

and the anhydrous salt—

	I.	II.
Baryta	51·009	51·366
Molybdic acid } . .	48·991	47·530
Phosphoric acid }		1·104

These numbers almost coincide with those found with the neutral molybdate of baryta, described in the first part of this paper.

From the analyses of these salts and the phænomena described, it is quite evident that but a very small quantity of phosphoric acid is contained in combination with molybdic acid, and that its amount is apparently variable. Hence arises the question, What part does the phosphoric acid act in these compounds, and how are we to view the molybdic acid thus metamorphosed? Can we admit a different allotropic state in this molybdic acid? and should we distinguish it from the ordinary molybdic acid by the sign of *b*-molybdic acid?

We have made numerous experiments to convert molybdic acid into this different state by means of other bodies besides phosphoric acid. It is unnecessary to relate the experiments, as we came to the result, that, when perfectly pure molybdic acid was employed, in which the absence of phosphoric acid had been ascertained, no change could be effected. But the tendency of phosphoric acid to produce yellow precipitates or yellow solutions with molybdic acid is so great, that we look upon molybdic acid as the most sensitive test for phosphoric acid, since in cases in which we obtained mere indistinct signs of the presence of phosphoric acid by other reagents, the reaction with molybdic acid was quick and perfectly distinct.

Phosphoric acid, which acts so important a part both in the vegetable and animal organism, we have found, with the assistance of this reaction, to be most generally distributed in nature. All the rocks, all the felspars which we have examined, contain phosphoric acid, and to prove this by means of molybdic acid is exceedingly simple. The sulphuret of molybdenum which we used in our investigation was remarkably pure; only minute traces of gangue, consisting of fragments of quartz and felspar, were here and there perceptible, but the molybdate of ammonia prepared by roasting this mineral and exhaustion with ammonia contained a little phosphoric acid. To detect this impurity, it suffices to add to the concentrated solution of the salt an excess of muriatic or sulphuric acid, when instantly the solution assumes a yellow colour, and deposits in the course of a few minutes a yellow precipitate of *b*-molybdate (phosphomolybdate) of ammonia. Or if we take the alumina which has been obtained

in the analysis of any felspar, dissolve it in an acid, then add some pure molybdate of ammonia, and afterwards an excess of an acid, a copious yellow precipitate instantly falls. If we attempt to demonstrate the presence of phosphoric acid in the same alumina by a solution of magnesia (preventing the precipitation of the alumina by ammonia by the addition of tartaric acid), the reaction only occurs after several hours, and is then always very imperfect.

Phosphoric acid has so great a tendency to accompany molybdic acid in all its combinations, that we are unable to direct any other plan for procuring pure molybdic acid than by preparing an artificial sulphuret in the dry or humid way. In the decomposition of the potash double salt (obtained by acting with nitric acid upon a solution of molybdic acid in potash) by water, into trimolybdate of potash, which separates, and a neutral salt which remains in solution, traces of phosphoric acid accompany the insoluble compound. The presence of the phosphoric acid in this salt is best proved by converting it into the silver salt. On decomposing this salt with muriatic acid, separating the chloride of silver and evaporating the filtered solution, with the addition of a few drops of ammonia, a yellow precipitate of the ammonia salt is always formed: its amount is very small, and it has no influence upon the analysis; but it is quite sufficient to show the presence of the phosphoric acid.

III. *Determination of the Atomic Weight of Molybdenum.*

We shall here describe a large number of experiments which we have made in order to determine accurately the atomic weight of this metal. Although most of these experiments have not led to the desired result, they will nevertheless be of scientific interest. If, from their not being so accurate as we had reason to expect, they did not assist in fixing the atomic weight,—and exhibited in several instances differences from the theories previously admitted,—they nevertheless remain quantitative results, which show in what manner various compounds of molybdenum behave towards different reagents.

The atomic weight of molybdenum was ascertained by Berzelius in 1818, by precipitating a certain quantity of nitrate of lead with neutral molybdate of ammonia, and calculating the atomic weight from the quantity of molybdate of lead thus obtained. Berzelius, however, says of this determination, “that it is far from being trustworthy, and the number found is far more erroneous than the atomic weight of chromium ascertained in the same manner. The atomic weight of mo-

lybdenum requires, therefore, further experiments. It is probable that molybdic acid may be reduced by hydrogen, and then the atomic weight might be obtained with tolerable accuracy, especially if the acid after being weighed was saturated with ammoniacal gas to prevent its volatility, the ammonia salt decomposed by heat, and the residual fixed oxide ignited in hydrogen."

It is seen, therefore, that Berzelius places no great reliance upon his determination, which, moreover, is based upon one single experiment; and it is remarkable that he should have deduced the number 596.101, which differs but very little from the atomic weight we have found. As Berzelius points to the reduction of molybdic acid by hydrogen, we began with this experiment; we shall now proceed to describe it.

Action of Hydrogen upon Molybdic Acid.

Experiment I.—Molybdic acid was heated in a reduction-tube in a current of dry air, to deprive it of all moisture, and to be certain that the whole of the molybdenum was in the state of molybdic acid. We may observe that molybdic acid is not a very hygroscopic substance.

3.0388 grms. of this molybdic acid were heated in a current of hydrogen over an ordinary spirit-lamp. Reduction immediately ensued, a large quantity of water was given off, which, however, soon decreased, and in the course of an hour and a half had almost entirely ceased. When this point had been attained, the tube was allowed to cool, the hydrogen in it expelled by dry air, and the residue weighed; it amounted to 2.6846 grms., and was reddish-brown. Upon this the reduction was continued with an Argand lamp, when again considerable quantities of water were given off; and although the reduction was continued for eight hours under these conditions there was still a deposit of water. By this continued intense red heat the glass had gradually become so brittle and crystalline that the tube on cooling cracked. The contents of the bulb were partly brown, partly gray, and had a metallic lustre. The acid employed for the experiment had lost, according to the first weighing, 0.3548 oxygen, or 11.656 per cent.; but this result agrees tolerably well with the supposition that the molybdic acid, on reduction with hydrogen at a low temperature, loses 1 atom oxygen and is converted into the oxide which Berzelius calls oxide of molybdenum. But it may also be conceived that 2 atoms molybdic acid = 2MoO^3 are converted into molybdate of the

protoxide of molybdenum = MoO , MoO^3 . Admitting this, 100 parts of molybdic acid should furnish—

	<i>a.</i>	<i>b.</i>	Found.
Molybdic oxide	88·751	88·582	88·344

Experiment II.—2·1927 grms. molybdic acid were exposed for nine hours in a current of hydrogen to the most intense red heat that a lamp with double draught is capable of furnishing. The loss in this case amounted to 0·3793 or 17·298 per cent., and the substance in the bulb had throughout a gray metallic colour, which exhibited merely in the centre of the mass some spots of brown. The loss supposes that 2 at. molybdic acid = 2MoO^3 have been reduced to the state of MoO , MoO^2 ; this formula may also be written Mo^2O^3 , and it then corresponds to a sesquioxide, such as we find in many metals. It may also be assumed that 4 at. MoO^3 have been converted into 2MoO , MoO^3 , which agrees better with the preceding experiment and with what occurs in treating the acid salts of potash and soda with hydrogen. Whichsoever of these views is admitted, the calculated result always remains the same; and 100 parts of molybdic acid furnish—

<i>a.</i>	<i>b.</i>	Found.
83·126	82·873	82·702

If in this experiment 2 at. molybdic acid have lost 3 at. oxygen, and have become converted into the compound Mo^2O^3 , then the atomic weight of molybdenum is 567·137, which does not differ much from the atomic weight we have arrived at. We did not repeat these experiments, as for various reasons they cannot yield results sufficiently accurate to base thereupon the determination of the atomic weight. We are, however, perhaps justified in concluding from the experiments just described, that molybdic acid exposed to the reducing influence of hydrogen, at the highest temperature which glass is capable of bearing, cannot be reduced to the state of metal, but only to the lowest oxide.

Experiments with Sulphuretted Hydrogen.

Although the treatment of molybdic acid and of the neutral and trimolybdate salts of potash with sulphuretted hydrogen gas did not lead to the desired object, they nevertheless present various interesting phenomena.

2·739 grms. of dried and ignited molybdic acid were exposed in a reduction-tube to the reaction of dry sulphuretted hydrogen. As soon as the gas came into contact with the acid, heat was evolved and the colour of the acid changed to black, but this soon stopped. If the bulb is now heated,

there is immediately a disengagement of water ; and the action of the sulphuretted hydrogen is so energetic, that when the current of gas is not too rapid, all the sulphuretted hydrogen is absorbed. The experiment lasts very long ; at first a small spirit-lamp suffices, but gradually the temperature must be increased, and, finally, the strongest heat which an Argand lamp can give must be used. It appears that at first an oxysulphuret is formed, which is very difficult to decompose. After the operation had been continued for twenty-one hours, no further formation of water could be observed ; but nevertheless no two weighings agreed. The difference between two weighings amounted to as much as 0.0006 gm. At the time we were unable to explain the cause of these differences, but we subsequently discovered it and shall allude to it in the following experiments.

When the reduction-tube had become perfectly cold, the sulphuretted hydrogen in it was expelled by dry air, and it was then weighed as quickly as possible ; two successive weighings gave 3.0545 and 3.0551 grms. ; the mean of the two is 3.0548.

Assuming that in this experiment the whole of the molybdic acid has been converted by the action of the sulphuretted hydrogen into sulphuret of molybdenum MoS^2 , we find the atomic weight of molybdenum by the following equation, in which the atomic weight of sulphur is admitted to be 200.75, and also 200 :

$$2.739 : 3.0548 = x + 300 : x + 401.5$$

$$x = 580.336 ;$$

or

$$2.739 : 3.0548 = x + 300 : x + 400$$

$$x = 567.231.$$

If this result is compared with the theoretical calculation, 100 parts of molybdic acid should yield—

	<i>a.</i>	<i>b.</i>	Found.
Sulphuret of molybdenum	111.416	111.416	111.529

We made a similar experiment with molybdic acid which had been prepared from native sulphuret from a different locality, when 2.855 grms. molybdic acid gave 3.1652 sulphuret of molybdenum, or 110.865 per cent. Even though this experiment is not perfectly in accord with the preceding one, it at all events proves the identity of different molybdic acids.

Experiment with Neutral Molybdate of Potash.

Calcined neutral molybdate of potash was heated in a current of dry air in a counterpoised reduction-tube, weighed after cooling, and then connected with a sulphuretted hydrogen apparatus. The dry sulphuretted hydrogen acted instantly, and with considerable evolution of heat, upon the potash salt, water was formed, and the salt assumed an orange-red and gradually a dark reddish-brown colour. After some time the reaction ceased, the bulb became cold, and it was now gently heated with a small lamp; a considerable disengagement of water immediately ensued, and the sulphuretted hydrogen was so rapidly absorbed that not a bubble passed through the apparatus. It is necessary to raise the temperature gradually towards the end, that the entire mass may be incandescent: a portion of the contents fuses. At the commencement the action of the sulphuretted hydrogen is very energetic, but it soon decreases and proceeds very slowly, so that much time elapses before no further formation of water is perceptible. On attaining this point the bulb was allowed gradually to cool, and here a peculiar phenomenon occurred,—as soon as the bulb had acquired a certain lower temperature, the whole of the sulphuretted hydrogen was absorbed by the mixed sulphurets: not a single bubble past through for some time. This condensation of the sulphuretted hydrogen we first observed in making this experiment; it is probable, however, that the differences in the weighings in the former experiment were owing to the same cause.

As this condensation must give rise to an error, we expelled the sulphuretted hydrogen by a current of dry carbonic acid, keeping the bulb at a gentle heat; but although we passed carbonic acid through the tube for an hour, sulphuretted hydrogen was constantly given off, but not a trace of sulphurous acid was perceptible. As this led to our object, we expelled the sulphuretted hydrogen, immediately after the cooling, by dry air, and then weighed it as quickly as possible. At the end of the experiment the contents of the bulb were fused partly to a reddish-brown mass, which had acted very much upon the glass, and a portion had formed a mass with a plumbiferous hue. The contents were now treated with water, which gave an orange-red solution, while sulphuret of molybdenum, Mo S_2 , separated; it was collected upon a filter, washed, dried at 212° , and its weight determined. On evaporating the filtered solution, and slow crystallization, we obtained the beautiful compound described by Berzelius under the name of sulphomolybdate of potassium; but besides these crystals the

microscope detected in the mother-liquor a salt which separated in white, minute rhombohedrons.

Experiment I.—2·1188 grms. neutral molybdate of potash furnished on treatment with sulphuretted hydrogen 2·9167 grms., in which were contained 1·081 grm. sulphuret of molybdenum.

Experiment II.—1·1305 grm. neutral salt furnished 1·582 grm. sulphurets.

Consequently 100 parts of the neutral molybdate of potash furnish—

	I.	II.
Sulphurets	137·658	136·753
in which is contained, according to experiment I., 51·019 per cent. sulphuret of molybdenum, MoS^2 .		

Experiment with Trimolybdate of Potash.

Sulphuretted hydrogen does not act upon the trimolybdate of potash in the cold, but if the apparatus is warmed, water is instantly disengaged and sulphur absorbed. The same phenomena occur as in the preceding experiment; after sulphuretted hydrogen had been passed for ten hours over the salt, and two successive weighings exhibited but a slight variation, we looked upon the experiment as terminated, especially as in this case the glass was very much acted upon by the partially fused mass. In this case we also treated the mass with water and estimated the sulphuret of molybdenum.

2·5117 grms. trimolybdate of potash furnished 3·030 sulphurets, which contained 2·1656 grms. sulphuret of molybdenum.

100 parts of the trimolybdate consequently furnish 120·635 sulphurets, in which are contained 86·221 parts MoS^2 .

The quantitative results which we have obtained in these three experiments it is difficult to explain and to connect with any theory. This is not merely owing to the bulb of the reduction-tube being so acted upon by the partially fused mass that the values are thereby rendered uncertain, but rather to the phenomena of decomposition being more complicated, so that to obtain a complete explanation it would be requisite to have likewise a quantitative determination of the sulphosalts and metallic sulphurets extracted by the water. However, as this would lead us far from the special object of this investigation, we did not make this quantitative examination, especially as we must then have entered upon new questions, for instance, what phenomena take place, and what combinations are formed in the treatment of potash or carbonate of potash with sulphuretted hydrogen at a high tem-

perature, and how the compounds so produced behave when heated in a current of carbonic acid.

The only result which we are at present able to deduce from these experiments is, that although sulphuret of potassium is present, the molybdenum cannot be obtained in the state of tersulphuret (MoS^3), but that a portion is converted into bisulphuret (MoS^2), whilst at the same time a portion of the potassium is converted into a higher sulphuret, and that a certain excess of a higher sulphuret of potassium is requisite to form a certain quantity of sulphomolybdate of potassium, and to retain it as such.

Experiments to determine the Atomic Weight of Molybdenum by fusing Molybdic Acid with Carbonated Alkalies.

If only a neutral salt were produced on fusing molybdic acid with an excess of carbonated alkali, the atomic weight of molybdic acid and of molybdenum could be deduced in a very simple manner from the amount of carbonic acid expelled. Starting from this assumption we made the following experiments:—

I. 2·180 grms. molybdic acid fused with 10·1007 grms. carbonate of potash, lost 0·6866 carbonic acid.

II. 1·7112 grm. molybdic acid fused with 10·9066 grms. carbonate of potash, lost 0·5369 carbonic acid.

III. 3·135 grms. molybdic acid fused with 9·3958 grms. carbonate of soda, lost 0·9866 carbonic acid: accordingly, 100 parts molybdic acid expel,—

	I.	II.	III.
Carbonic acid . .	31·4954	31·3749	31·4705

And if we calculate from this the atomic weight of molybdenum, assuming the atomic weight of carbon to be 75·12 (α), or 75·00 (β), we have, according to—

	α .	β .
Experiment I.	573·524	573·143
Experiment II.	576·858	576·476
Experiment III.	574·216	573·834
Mean . .	574·866	574·484

These experiments were made in the following manner: the alkaline carbonate was heated to redness in a platinum crucible, and after cooling over sulphuric acid, weighed. This was repeated until two successive weighings entirely agreed. In another counterpoised crucible the amount of molybdic acid was weighed off, and a large excess of the alkali shaken into the crucible containing the molybdic acid, the whole mixed with a small platinum wire which had been previously coun-

terpoised with the crucible, and the wire left in the crucible. The crucible with the residual alkali was heated to redness and weighed to see how much had been taken for the experiment. The crucible with the mixture of molybdic acid and carbonated alkali was now exposed to a slowly-increased heat, and as soon as the mass was perfectly liquid, the temperature was raised as high as it was possible with an Argand lamp and chimney. This heat was continued for half an hour, when the crucible was allowed to cool over sulphuric acid; the difference in weight gave the quantity of carbonic acid expelled. This ignition, cooling and weighing, had to be repeated five to six times with every experiment, and we took the average of all these weighings as being nearest to truth. The reason why we were compelled to take the average of the weighings is, that no two successive weighings were found to agree, there being sometimes an increase, at other times a decrease in weight. We are not able to explain the phenomenon, but it cannot be ascribed to the uncertainty of the balance, for this does not amount to more than $\frac{1}{10}$ th of a milligramme.

Although these experiments have led to an atomic weight for molybdenum which agrees very well with one arrived at by another method, we cannot, on account of the variations in the weighings, place perfect confidence in the experiments.

Experiments with Chlorine Compounds.

We hoped to arrive at good results by the preparation and examination of the chlorine compounds of molybdenum; in this we have not succeeded, it being very difficult to obtain any one of the chlorine compounds perfectly pure. Besides, phenomena occurred which had not been previously observed and investigated; and, finally, we found it to be perfectly impossible to determine the chlorine accurately in the form of chloride of silver.

Although for these reasons we have not followed up the subject further, we shall describe our observations, as they are not without interest. Oxide of molybdenum, prepared by calcining a mixture of molybdate of potash with an excess of chloride of ammonium and subsequent exhaustion with water, had sometimes a brown, sometimes a gray metallic colour, according to whether a larger or smaller quantity of sal-ammoniac had been used; in general it consisted of a mixture of the two. This oxide was employed to prepare the biacichloride of molybdenum. For this purpose we used a glass tube furnished with two bulbs, about an inch apart; into one of the bulbs 4 grammes of the oxide were conveyed, and it was then heated quite gently in a current of hydrogen, to expel all humidity, and the tube connected with a chlorine

apparatus so that only dry chlorine gas could pass over the oxide. When the apparatus had become filled with chlorine gas at the ordinary temperature at which no action is exerted upon the oxide, we applied a very gentle heat to the bulb containing the oxide: chlorine was absorbed with great avidity; biacichloride of molybdenum was formed, which was driven by a very gentle heat into the other bulb. When in this manner the greater portion of the oxide had been converted into the volatile chloride, the bulb was allowed to cool, and a current of dry air then passed through the apparatus for some time, to expel all chlorine gas, and the bulb containing the biacichloride melted off. This portion of the tube and its contents was weighed, the one extremity of the fused tube cut off, the contents dissolved in water, and after the tube had been well washed with water, dried and weighed, the loss furnished us with the amount of biacichloride taken for analysis. This chloride is readily soluble in water, but gave a faintly opalescent solution. When the solution had been very much diluted with water, we added a small quantity of nitric acid and then some nitrate of silver. At first pure chloride of silver fell, readily recognisable from its colour and external appearances; but on adding some more of the silver solution, the precipitate became very bulky and assumed a yellowish colour. On heating the solution, to cause the chloride of silver to subside and to dissolve the molybdate of silver which had been precipitated with it in the nitric acid, the liquid became more and more turbid, the precipitate increased, and the liquid, after twenty-four hours standing, still remained turbid. We now filtered, but with the precaution of pouring only the liquid on the filter; and after the precipitate had been washed several times in the beaker with hot water containing nitric acid, the whole was dissolved in dilute ammonia, and then nitric acid again added. These operations of dissolving, precipitating, and reprecipitating were repeated several times, for this was the only way of separating the whole of the molybdate of silver; finally, the chloride of silver was poured upon the filter and determined in the usual manner.

3.0881 grms. of biacichloride of molybdenum furnished 4.3245 chloride of silver = 1.069 chlorine.

If we compare the per-centage composition according to analysis and theory, we have—

	<i>a.</i>	Calc.	<i>b.</i>	Calc.	Found.
2 at. Molybdic acid.....	1777.932	48.095	1751.658	47.895	
1 at. Molybdenum	588.966	15.932	575.829	15.744	
6 at. Chlorine	1329.840	35.973	1329.840	36.661	34.622
	3696.738	100.000	3657.327	100.000	

H. Rose, who first quantitatively examined this compound and determined its formula, found in two analyses 34.295 and 35.001 per cent. chlorine.

This biacichloride of molybdenum forms yellowish-white shining laminæ, which exhibit no crystalline form even with a compound microscope.

We have prepared the biacichloride according to this method several times, but have never noticed the simultaneous appearance of any other chlorine compound. Although it is difficult to determine accurately the chlorine, owing to the molybdate of silver accompanying the precipitate, yet we believe that the principal source of uncertainty is to be ascribed to the difficulty of preparing pure biacichloride. This compound is generally mixed with traces of molybdic acid, for when perfectly pure, in which state it is only accidentally and very rarely obtained, it dissolves entirely in water, while in general it furnishes an opalescent solution. If this is the correct cause, it is readily explained why H. Rose, as well as ourselves, have found so small an amount of chlorine in the compound. This explanation is further confirmed by the circumstance, that when dry hydrogen is passed over the biacichloride and the bulb gently heated, nearly the whole of the chlorine compound is volatilized; but a small residue is left, which most probably consists of the molybdic acid contained in the biacichloride.

As we could not obtain a satisfactory result from the analysis of the biacichloride, we made the following experiment to obtain some other chloride.

A glass tube about 2 feet long, curved somewhat anteriorly, was filled, first with a considerable stratum of well-calcined fragments of charcoal, and then with a mixture of molybdic oxide and charcoal powder which had been previously well calcined; the straight end of the tube was connected with a chlorine apparatus, and dry chlorine passed for a considerable time through it. That part of the tube with the charcoal was now heated until the charcoal was incandescent, when the other portion of the tube containing the mixture was gradually heated to redness. The current of chlorine was continued during the whole operation; it was rapidly absorbed and various chlorine compounds formed, of which we were able to distinguish the following:—

The most volatile compound which condensed in the most anterior curved part of the tube was the biacichloride of molybdenum; the quantity was small; immediately behind this was the compound described by Berzelius under the name of chloride of molybdenum; it formed dark brown, shining cry-

stals resembling iodine. The fragments of charcoal were coated with a black crust; and on allowing the tube to cool, its whole length was covered with a yellowish crystalline mass which did not appear to be very volatile. Of these compounds, which we will designate by the letters A, B, C, and D,

A consists of biacichloride, gives a clear solution with water, and deliquesces in the air;

B appears in fine, dark brown, shining needles, gives with water a blue solution, from which ammonia precipitates a brownish red oxide;

C is not altered by exposure to the air, possesses a black colour, is very slightly and slowly acted upon by alkalies, and insoluble in water;

D is readily soluble in water; the solution gradually becomes blue, but nothing is precipitated by ammonia.

These statements, which are in the highest degree imperfect, are merely intended to show that we know very little of the chlorine compounds of molybdenum, and that the subject requires a thorough investigation.

Experiments with Sulphuret of Molybdenum.

Starting from the fact that sulphuret of molybdenum, when heated with sufficient access of air, is gradually oxidized and converted into molybdic acid, we imagined that if we were able to prepare artificially a pure sulphuret of molybdenum with exactly the same composition as the native mineral, and converted this by roasting completely into molybdic acid, which remains, and into sulphurous acid, which is volatilized, it was to be expected that an accurate atomic weight of molybdenum might be calculated from the difference in weight of the sulphuret of molybdenum employed. No objection can be urged to this method *à priori*; it is simple, and the simpler an analytical method the more certain the result in general. If we assume that the oxidation can be effected completely, the method consists in three weighings:—1, counterpoising the glass tube in which the roasting is to be effected; 2, weighing with the pure sulphuret of molybdenum; and 3, weighing the molybdic acid obtained. We shall now prove that our theory was correct, and that we have succeeded in determining with certainty the atomic weight of molybdenum based upon the atomic weight of sulphur.

The artificial sulphuret of molybdenum was prepared according to the method described in the first part of this investigation for obtaining pure molybdic acid, with this difference only, that the sulphuret was dried over sulphuric acid under

the air-pump. If this precaution is omitted, by drying it in the air or at 212° , the sulphuret always exhibits an acid reaction, owing to the formation of some sulphate of the protoxide of molybdenum. It soon dried under the air-pump, where it was kept until no further loss in weight could be observed. We thus prepared two different quantities of sulphuret of molybdenum, using the following proportions:—

For sulphuret A we fused together 4 grms. molybdic acid, 8 grms. sulphur, and 6 grms. carbonate of potash; for the sulphuret B we used 11 grms. trimolybdate of potash, 20 grms. sulphur, and 6 grms. carbonate of potash.

After we had thus prepared a pure sulphuret, the experiments were made in the following manner:—a glass tube provided in the centre with a bulb was stopped at one end with a little asbestos, and the whole then heated to redness in a current of dry air, and when cold counterpoised and the sulphuret of molybdenum weighed in it. Upon this the bulb with its contents was heated in a current of dry hydrogen, when a small quantity of water was expelled, but we were never able to observe any disengagement of sulphurous acid. But if the sulphuret of molybdenum had not been dried under the air-pump, there was always some sulphurous acid liberated on heating it in hydrogen. When the sulphuret had been perfectly dried in this manner, the hydrogen was expelled after cooling by dry air and the weight of the sulphuret again determined. The difference between the first and second weighing never amounted to more than from 1 to 2 milligrammes at the furthest. That part of the glass tube in which the asbestos was, was connected with an aspirator, and the bulb heated gently with a small spirit-lamp, ordinary moist atmospheric air, and only at the end of the operation dry air being allowed to pass over the sulphuret. This operation does not require a very high temperature, but the contents of the bulb must be frequently shaken, so as constantly to present fresh surfaces to the reaction, in order that the mass may not cake into one lump. If these precautions are neglected, a portion of the molybdic acid encloses some undecomposed sulphuret and prevents the complete oxidation, as we shall show further on. If dry air is allowed to act upon the sulphuret from the very beginning of the operation, the roasting is just as complete, but it is slower. The operation, when from 1 to 2 grammes of sulphuret is employed, lasts from two to three hours. It is not advisable to employ larger quantities, as the oxidation is then effected with greater difficulty, and it is impossible to be certain that no portion has escaped decomposition. When the sulphuret was converted into the yellow molybdic acid we

passed dry air through the tube, first with the application of heat, and afterwards when it had cooled ; it was then weighed. This operation of roasting was repeated twice, each time for half an hour, to be certain that the oxidation was complete. The difference in the weight between the first and third weighing never amounted to more than half a milligramme, and the second and third weighings always coincided.

To convince ourselves finally that the whole of the sulphuret had been really converted into molybdic acid, we dissolved the acid in ammonia, and always obtained a perfectly clear solution. The following are the experiments.

Sulphuret of Molybdenum A.

		gram.		per cent.
I.	1.3558	gram. MoS ² gave 1.2174	molybdic acid =	89.7919
II.	1.329	89.7291

Sulphuret B.

III.	1.487	gram. MoS ² gave 1.333	molybdic acid =	89.6436	...
IV.	1.4225	...	1.2761	...	89.7082
V.	1.403	...	1.2637	...	90.0712
VI.	1.268	...	1.1416	...	90.0315
VII.	1.2947	...	1.1622	...	89.7660
VIII.	1.4957	...	1.3426	...	89.7640
IX.	1.299	...	1.1652	...	89.9272
X.	1.1138	...	1.0009	...	89.8635

We must exclude from this series of experiments as erroneous V., VI. and IX., the shaking having been omitted.

If we compare the other seven experiments and take the average, we find that 100 parts of sulphuret give 89.7523 molybdic acid. But before we proceed to draw further conclusions from these experiments, we must first show that the artificial sulphuret used in these experiments has the same constitution as the native mineral. For this purpose we have analysed specimens of native sulphuret from two different localities in Sweden; the one was from Lindås in Småland, and the other from the district of Bohus. The analyses were likewise made by roasting, and when this was finished the molybdic acid dissolved in ammonia, when the insoluble gangue was left behind and could thus be estimated : of the sulphuret from Lindås we made three determinations, viz.—

I.	1.4847	gram. native sulphuret gave 1.3382	molybdic acid & 0.0427	gangue.
II.	1.400	...	1.2599	...
III.	2.247	...	2.0235	...
IV.	1.371	native sulphuret from Bohus gave 1.2348	gram. molybdic acid and	0.0430

We have moreover examined the artificial sulphuret obtained by treating the neutral molybdate of potash with sulphuretted hydrogen.

V. 0·3432 grm. sulphuret gave 0·3064 molybdic acid.

If we deduct the quantities of gangue found in the native sulphurets of molybdenum, 100 parts of native sulphuret yield, according to—

I.	. . .	89·841
II.	. . .	89·912
III.	. . .	89·943
IV.	. . .	89·744
V.	. . .	89·277

and these results prove beyond a doubt the identity of the native sulphuret, and the artificial sulphuret of molybdenum. If we calculate the per-centage composition of the sulphuret of molybdenum according to theory, it consists of—

	<i>a.</i>	Calc.	<i>b.</i>	Calc.
1 at. Molybdenum	588·966	59·464	575·829	59·009
2 at. Sulphur . .	401·500	40·536	400·000	40·991
	990·466	100·000	975·829	100·000

The analyses give, after deducting the gangue, for the native sulphuret the following results:—

	Lindas, I.		Lindas, II.	
	<i>a.</i>	<i>b.</i>	<i>a.</i>	<i>b.</i>
Molybdenum .	59·522	59·067	59·569	59·114
Sulphur . .	40·478	40·933	40·431	40·886

	Lindas, III.		Bohus, IV.	
	<i>a.</i>	<i>b.</i>	<i>a.</i>	<i>b.</i>
Molybdenum .	59·588	59·133	59·458	59·004
Sulphur . .	40·412	40·867	40·542	40·996

It is evident that the gangue in the sulphuret of molybdenum is a mere mechanical impurity, from its quantity varying in the mineral. If in calculating the analyses we take the gangue into consideration, we find—

	I.	II.	III.	IV.
Gangue. . .	2·876	0·800	1·1215	3·1364
Molybdenum .	57·368	58·627	58·4700	57·1534
Sulphur . .	39·756	40·573	40·4085	39·7102

These analyses differ from those made by Buchholz, Brandes, and Seybert; but these chemists never determined accurately the amount of gangue in the native sulphuret, and, moreover, the atomic weight employed by them was less certain.

Having shown the identity of the native and artificial sulphuret of molybdenum, we will now return to the first experiments of roasting the artificial sulphuret, where we found that 100 parts sulphuret (MoS_2) furnished 89·7523 parts molybdic acid. This result is founded solely upon experi-

ments; but if, starting from this, we wish to calculate the atomic weight of molybdenum, it must be based upon the number representing the atomic weight of sulphur. Berzelius determined the atomic weight of sulphur to be 200·75, by converting a known weight of chloride of silver into sulphuret. Erdmann and Marchand have arrived at the number 200·000 by the analysis of the sulphuret of mercury. The starting-point for Erdmann and Marchand's number is not only dependent on the atomic weight of mercury, but the most important question is, Were these chemists perfectly certain that the sulphuret of mercury was free from any mechanical admixture of metallic mercury? As this was not ascertained, we do not think that the atomic weight of sulphur found by them, although highly probable, can be admitted unconditionally. With regard to Berzelius's atomic weight for sulphur, it is liable to the objection, that perhaps a minute quantity of chloride of silver surrounded by sulphate of silver was withdrawn from the action of the sulphuretted hydrogen. We therefore treated 5·5967 grms. chloride of silver with sulphuretted hydrogen and obtained 4·8395 sulphuret of silver. Whence, admitting Berzelius's atomic weights for chlorine and silver, that of the sulphur is found to be 200·71; but on dissolving the sulphuret of silver in pure nitric acid, a small quantity of undecomposed chloride of silver remained undissolved, and, consequently, the number 200·71 must be too high. We wished to decide this important question, but have been prevented by various circumstances, and, on that account, all the theoretical calculations we have made, and also that of the equivalent of molybdenum, have been calculated with the two different atomic weights for sulphur.

Now, if we calculate the equivalent of molybdenum from the quantity of molybdic acid which we obtained from 100 parts of sulphuret of molybdenum, we have, when the atomic weight of sulphur is assumed to be 200·75,—

$$100 : 89.7523 = x + 401.5 : x + 300$$

$$x = 588.966 \quad , \quad . \quad . \quad . \quad . \quad . \quad (a.)$$

and when the atomic weight of sulphur is 200·000,—

$$100 : 89.7523 = x + 400 : x + 300$$

$$x = 575.829 \quad . \quad . \quad . \quad . \quad . \quad . \quad (b.)$$

Although the difference between the two atomic weights here assumed for sulphur is not very great, its influence in calculating the atomic weight of molybdenum is very considerable, the difference between a and b amounting to more than 13

units, consequently to more than 1 entire equivalent of hydrogen. That the equivalent a must be too high is not merely evident from the objections which we have made respecting the atomic weight of sulphur, but is also confirmed by the following circumstances :—

I. Without laying too great stress upon the reduction of molybdic acid by hydrogen, we may nevertheless direct attention to experiment II., this agreeing much better with the numbers calculated according to the atomic weight b , than according to a .

II. The analyses of the trimolybdate of potash, the only salt which can be obtained perfectly pure, agree much better with the numbers calculated according to b , than with those according to a .

III. The most decided proof for the lower atomic weight of molybdenum is derived from the results of the experiments of fusing molybdic acid with carbonated alkalis. These results agree with each other, and likewise with the atomic weight b very well. The atomic weight deduced from these experiments is founded upon that of carbon, which it may be admitted is determined as accurately as possible in the present state of chemistry. Even should a small uncertainty exist with respect to this number, it would have very little influence upon the atomic weight of molybdenum. We therefore consider ourselves justified in drawing the conclusion, that the atomic weight of molybdenum is 575.829, and the per-centage composition of molybdic acid

Mo 65.714,
O 34.286.

LXXVII. *On a Property of the Hyperbola.*

To the Editors of the Philosophical Magazine and Journal.

GENTLEMEN,

THOUGH I am but an equation, and as such, more accustomed to be solved than to solve, I cannot any longer endure the injustice which is done to me with respect to the curves I have the honour to control. Want of long suffering cannot be imputed to me, or to any of my species; we even carry the Christian maxim further than the Christian law requires: for in what manner soever any one smites us on one cheek, we not merely turn to him the other also, but insist upon his treating it in the same manner, and cannot be satisfied until it is done. Coupled as we are with the very notion of justice (for what do the scales represent but an equation be-