

XII. *An Analysis of the Carinthian Molybdate of Lead; with Experiments on the Molybdic Acid. To which are added some Experiments and Observations on the Decomposition of the Sulphate of Ammoniac.* By Charles Hatchett, Esq. Communicated by Sir Joseph Banks, Bart. K. B. P. R. S.

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§ I.

THE celebrated SCHEELLE, in 1778, read before the Academy of Sciences at Stockholm an essay, in which he proved, by a series of ingenious experiments, that the mineral called *Molybdæna* was composed of sulphur, and a peculiar metallic substance, which, like arsenic and tungsten, was liable by superoxygenation to be converted into a metallic acid, which in its properties differed from any other that had been previously discovered.*

The experiments of Mr. LE PELLETIER,† Mr. ISLMANN,‡ and Mr. HIELM,§ confirmed the discovery of the Swedish chemist; but the existence of this metallic substance was only known to be in that mineral which SCHEELLE had examined, as no vestige of it had as yet been discovered in other bodies ap-

* SCHEELLE'S Essays, translated by Dr. BEDDOES, p. 227.

† *Journ. de Physique*, Decembre, 1785.

‡ *Chemische Annalen von CRELL*, 1787, et *Journ. de Physique*, Octobre, 1788.

§ *Journ. de Physique*, Mai, 1789.

pertaining to the mineral kingdom. Mr. JACQUIN, in 1781 and 1786, gave to the public an account, from the Abbé WULFEN, of a yellow sparry lead ore, found at Villach in Carinthia;* and the Abbé WULFEN himself, in an elaborate work, written in the German language, and published in 1785, also described the abovementioned lead ore, together with some experiments which had been made on it.†

Nothing satisfactory, however, relative to its nature was exposed in these memoirs; and although the substance was indisputably proved to be an ore of lead, yet the mineralizing principle of it remained unknown.

In 1790, Mr. HEYER, of Brunswick, made some experiments on this ore, from which he inferred that it was composed of lead, combined with the tungstic acid;‡ and in the same year Mr. KLAPROTH communicated to Dr. CRELL a similar account, which he had received from Mr. SALZWEDEL, of Frankfurt sur Mayne.§

This substance was therefore universally believed to be a tungstate of lead, till that excellent chemist Mr. KLAPROTH undertook to subject it to a farther examination; and as the experiments which I have made may be regarded as a continuation of those made by Mr. KLAPROTH, I think it necessary here to mention them.

* NICOLAI JOSEPHI JACQUIN *Miscellanea Austriaca*, Tom. II. p. 139; et N. J. JACQUIN *Collectanea*, Tom. I. p. 3.

This ore is also described in *Lithophyl. Bornianum*, Tom. I. p. 90; et Tom. II. p. 123.—KARSTEN in *Mus. Lesk.* Tom. II. p. 501.—WERNER's *Verzeich.* Band, I. p. 128.—RAAB's *Catal.* Tome II. p. 379.—*Romé de l'Isle Cristal.* Tome III. p. 387.—WIDENMANN's *Handbuch der Mineralogie*, p. 864.

† XAVIER WULFENS *Abhandlung vom Kärnthnerischen Bleyspate.* Wien, 1785.

‡ *Chemische Annalen von CRELL*, 1790, p. 58.

§ *Ibid.* 1790, p. 297.

Mr. KLAPROTH says, that by previous experiments he had found, that nitric acid much diluted did not attack the ore when cold ; and therefore to separate it from the soluble matrix, he successively poured small quantities of the diluted acid on the ore till all effervescence had ceased, after which the ore was washed and dried. The nitric acid which had been employed was found to contain calcareous earth, and also a considerable quantity of red oxyde of iron, which upon being dissolved in sulphuric acid, left a residuum of lead and siliceous earth.*

Two drachms of the purified ore were mixed with an equal quantity of pot-ash, and afterwards exposed to the fire in a crucible. The mixture melted without intumescence. When cold, the mass was of a reddish colour, and the surface was covered with small scales. Water was poured on it, and the solution was saturated with nitric acid. The following day, the bottom of the glass was found covered with projecting crystals, about a quarter of an inch in length : these crystals were formed of small glittering rhomboidal plates, heaped one on the other. Their flavour was rather metallic. They quickly melted with the blow-pipe, on charcoal, without any increase of bulk, and became small round drops, which were immediately absorbed by the charcoal. When melted by the blow-pipe in a silver spoon, they appeared as small grains, of a greyish colour, which became streaked in cooling, and deposited a white powder during the operation.

When the phosphate of ammoniac and soda was melted, and some of these crystals were added, they speedily dissolved,

* *Analyse Chimique du Plomb Spathique jaune de Carinthie. Annales de Chimie, 1791, pag. 103.*

and communicated to the salt a green colour, more or less deep according to the quantity employed.

They completely dissolved in distilled water, when heated.

Prussiate of pot-ash with this solution produced a reddish-brown precipitate, not very dark.

When some drops of muriatic acid were mixed with the solution of these crystals in water, and a small piece of tin was added, the liquor became of a deep blue.

The solution of muriate of tin poured on the crystals produced the same effect.

Mr. KLAPROTH from these experiments concludes, that the crystals are the acidulous molybdate of pot-ash, especially as the crystals obtained from the filtrated solution of the molybdæna of Altenberg, detonated with nitre, and saturated with nitric acid, have the same properties.

As in the above experiment the ore did not appear to have been completely decomposed, Mr. KLAPROTH mixed two drachms of the purified ore with ten of carbonate of pot-ash, melted the whole in a crucible, and reduced it to powder, and dissolved it in water.

The solution was filtrated, partially saturated with muriatic acid, and heated. A white precipitate fell, resembling curdled milk, which consisted of molybdic acid, and a still larger quantity of oxyde of lead. When dissolved in muriatic acid, the lead was precipitated in the state of muriate of lead.

This precipitate being separated by a filter from the alkaline solution partially saturated with muriatic acid, the solution was then completely saturated with the same acid, and again became slightly turbid, and deposited a white precipitate, which resembled starch in cold water. This precipitate,

after it had been washed and dried, was subjected to the same experiments as the abovementioned crystals, and exhibited the same properties, excepting that it did not dissolve in distilled water till some drops of muriatic acid were added.

When the solution was evaporated in a glass bason, the rest of the oxyde of molybdæna was deposited in the form of a heavy citron-coloured powder.

The white oxyde of lead on the filter through which the solution of the alkaline mass had passed, was found to be mixed with siliceous earth. When melted on charcoal, it did not entirely assume the metallic form, but a part changed into a small grain of transparent yellowish vitrified oxyde of lead. Mr. KLAPROTH observes, that in this experiment the presence of the siliceous earth prevented the complete reduction of the lead, in the same manner as when glass of lead, composed of three parts of oxyde of lead and one of siliceous earth, is melted upon charcoal. He therefore dissolved this oxyde in weak nitric acid, separated the siliceous earth by a filter, and precipitated the lead by sulphuric acid.

Mr. KLAPROTH, however, doubts whether the greater part of the siliceous earth was not introduced, during the operation, by the action of the alkali on the crucible.

A drachm of the ore was digested with a considerable quantity of nitric acid, and a great part was dissolved. In the solution white flocculi were perceived, and were separated by a filter. When dried they were like a membrane, which became bluish when exposed to the light, and much resembled the molybdic acid obtained from molybdæna, by repeatedly distilling nitric acid from it. In the filtrated nitric solution there was much oxyde of molybdæna mixed with oxyde of

lead. The lead was therefore precipitated by sulphuric acid, and afterwards the molybdæna by prussiate of pot-ash.

A drachm of the ore was digested with muriatic acid, and was completely dissolved, excepting a small residuum of siliceous earth. The solution was transparent, and without colour. In the course of some time it plentifully deposited crystals of muriated lead. When these crystals were separated, the solution was evaporated, and the interior of the bason was, during the evaporation, covered with a bluish saline crust, which dissolved and the colour disappeared when the vessel was shaken. The concentrated solution decanted from the muriate of lead (which had been precipitated during the evaporation) was of a deep blue, which disappeared when water was added. The solution was then saturated with alkali, and deposited a white precipitate, which consisted of molybdic acid, together with a small quantity of oxyde of lead.

According to these experiments Mr. KLAPROTH remarks, that the yellow sparry lead ore of Carinthia is composed of oxyde of lead and molybdic acid, and that this mineralogical novelty is the more remarkable, as it is the only one of the kind known at present. It is also worthy of notice, that the molybdæna changes its form according to the method employed to precipitate it from alkaline solutions; for it is obtained either in a crystalline form, or in that of a white powder, or in that of a citron-coloured oxyde. When crystallized, it is soluble in acids, and in water; as a white powder it does not dissolve in water, unless a small quantity of muriatic acid is added; but in the state of the citron-coloured oxyde, it is insoluble in water as well as in the acids. Mr. KLAPROTH considers that this difference is occasioned by the presence of

some alkali in the two first substances, so as to form an imperfect neutral salt with the molybdic acid, but that the yellow powder is in the state of a simple oxyde.

This yellow colour probably occasioned the supposition that the lead was mineralized by the tungstic acid; but the blow-pipe is sufficient to distinguish them. The yellow oxyde of molybdæna loses the colour as soon as the point of the flame touches it, inclines to an olive colour, and melts into small grains, which are immediately absorbed by the charcoal. In the phosphate of ammoniac and soda it dissolves, and communicates to it a green colour. On the contrary, the yellow oxyde of tungsten by ignition becomes blue or black, remaining refractory, and with phosphate of ammoniac and soda it produces a sky-blue glass.

Mr. KLAPROTH concludes his paper by saying, that he could not exactly determine the proportions of the ingredients, as the quantity of the ore in his possession was not sufficient to make the necessary allowance for the solubility of the oxyde of lead in the alkalies, and especially that of the molybdic acid when in a state of combination.

These experiments of Mr. KLAPROTH certainly prove that this ore is a molybdate of lead; but as the quantity which he had was too small, either to make a greater number of experiments, or a regular analysis, I was induced to attempt a further investigation of it; and therefore in the course of the last summer I made the experiments and analysis which are described in this paper.

§ II. *Characters of the Carinthian Molybdate of Lead.*

The molybdate of lead is found at Villach, in Carinthia.* The matrix is a limestone, of a pale brownish-grey colour, often more or less tinged with oxyde of iron.

The ore is a heavy brittle substance, easily scratched with a knife, and of a yellow, varying from pale yellow to orange colour.

The fracture is sparry.

The external lustre is like that of wax, and when crystallized, two of the faces of the crystals are commonly opaque, and of a pale yellow, but the remaining four faces or sides have a resinous appearance.

It generally exhibits an appearance of crystallization, and the crystals, when perfect, afford various modifications between the octoëdral figure and the cube.

The specific gravity of a specimen, from which I had separated all the visible part of the matrix, was 5092 (the temperature of the water being 60°), but when the ore was reduced to powder, and purified by diluted nitric acid, I found the specific gravity to be 5706.

1. When the ore was examined by the blow-pipe, it at first split and crackled as soon as the point of the flame touched it, but afterwards readily melted into a dark coloured mass, in which were some shining globules of lead.

2. With borax it formed a brownish-yellow globule, but when it was in a small proportion, and heated by the interior

* It is said to have been sometimes found in Austria and Hungary, but I doubt if the nature of these ores is the same.

flame, it occasionally produced a glass, which was greenish blue, and sometimes deep blue.

3. With phosphate of ammoniac and soda it formed a sea-green glass, which in proportion to the quantity of the ore sometimes became deeper in colour, so as to be nearly of a deep blue.

Before I made the following experiments, I reduced eight ounces of the ore to a fine powder, and dissolved the matrix after the manner of Mr. KLAPROTH, by successively pouring on the powder small quantities of nitric acid diluted with six parts of distilled water, after which I edulcorated and dried the residuum. The nitric acid used in this operation contained (as Mr. KLAPROTH has mentioned) calcareous earth, oxyde of iron, and oxyde of lead; but as prussiate of pot-ash produced a pale green precipitate, I suspected that some other metallic substance beside iron and lead was in the solution. I therefore added muriate of tin to a portion of it, which was immediately changed from a pale yellow to a pale blue, and shewed that a small quantity of molybdic acid was present in the solution.

§ III. *Molybdate of Lead with Water.*

I boiled twelve ounces of distilled water on twenty grains of the purified ore in a glass matrass during three hours. The ore did not appear to be changed, nor did the water after it had passed the filter afford any trace of matter in solution. I believe, therefore, that the molybdate of lead is insoluble in water.

§ IV.

As Mr. KLAPROTH had proved the action of the fixed alkalies on the molybdate of lead, in the dry way, I was desirous to know what effects they would produce in the humid way, and therefore made the following experiments.

EXPERIMENT I.

A. I boiled four ounces of strong lixivium of caustic potash with twenty grains of the purified ore, till there remained at the bottom of the matrass a dry mass, which was partly red, yellow, and green. I reduced this to powder, and poured distilled water on it, till the water came away without any taste.

The alkaline solution was filtrated, and afterwards saturated with sulphuric acid. The liquor then became turbid, and deposited a small quantity of a white precipitate, which consisted of lead and some molybdic acid. This was separated by a filter, and prussiate of pot-ash being added to the clear liquor, precipitated a great quantity of molybdæna, in the state of a reddish-brown flocculent precipitate.

B. I took the residuum of the alkaline solution (which now was chiefly of a red colour, and appeared like minium) and poured nitric acid, very largely diluted, on it till the whole was dissolved. I then precipitated the lead with sulphuric acid, and from the clear liquor which remained I afterwards, by the means of prussiate of pot-ash, obtained a quantity of Prussian blue.

EXPERIMENT II.

A. Twenty grains of the purified ore were boiled with four ounces of a lixivium of carbonate of pot-ash. When all the water was evaporated, there remained a white saline mass, which was reduced to powder, and treated with distilled water as in the former experiment.

A large quantity of a heavy white residuum remained on the filter.

The clear solution was saturated as before with sulphuric acid, and a white precipitate, similar to that of the former experiment, was obtained. This was separated, and a copious precipitate of molybdæna was produced, upon the addition of prussiate of pot-ash.

B. The white residuum was thenedulcorated, and when diluted nitric acid was poured on it, it was dissolved with effervescence. From this solution I precipitated the lead by sulphuric acid, and afterwards the iron by prussiate of pot-ash.

Ammoniac, when digested on the ore, had not any effect.

From these experiments it appears, that the molybdate of lead is decomposed by the fixed alkalies in the humid way, and that the component parts of the ore are lead and iron mineralized by the molybdic acid.*

* The alkalies, whether caustic or combined with carbonic acid, do not act in the humid way on molybdæna when mineralized by sulphur. SCHEELLE'S *Essays*, p. 230; and *Mémoire sur la Molybdène*, par M. PELLETIER, *Journ. de Physique*, Decembre, 1785, p. 437.

§ V. *Molybdate of Lead with Sulphur.*

A mixture, composed of fifty grains of the ore and 150 grains of sulphur, was put into a small glass retort, to which a receiver was luted.

The fire was then gradually raised till all of the sulphur was driven over, and the bottom of the retort began to melt.

The residuum was a black loose powder, which was greasy to the touch, and soiled the fingers like molybdæna.

This black powder was digested in a strong heat with nitric acid, diluted with three parts of water.

Nitrous fumes were discharged during the digestion, and the powder was dissolved, excepting a residuum of molybdic acid, which was of a greenish-yellow colour.

The solution was diluted with an equal quantity of distilled water, and was filtrated. Sulphuric acid was then added till all of the lead was precipitated; after which I obtained a brown precipitate by prussiate of pot-ash.*

§ VI. *Molybdate of Lead with Carbonate of Ammoniac.*

A mixture, composed of 50 grains of the ore and 220 of dry carbonate of ammoniac, was put into a glass retort, and was sublimed with a gentle heat.

The molybdate of lead remained in the retort without having suffered any apparent alteration.

The ammoniac, however, had raised a small portion; for

* As the quantity of molybdic acid in the ore is much greater than that of iron, it is scarcely possible to discover the latter when they are precipitated together by prussiate of pot-ash.

when it was dissolved in distilled water, and was saturated with an acid, prussiate of pot-ash produced a brown cloud.

§ VII. *Molybdate of Lead sublimed with Muriate of Ammoniac.*

EXPERIMENT I.

A mixture of 50 grains of the molybdate of lead and 240 grains of muriate of ammoniac was sublimed.

The sublimate was partly yellow, green, and blue; there was also some muriatic acid, and the residuum was a black powder.*

A. The sublimate was mixed with an equal weight of sulphur, and distilled.

The residuum of this was a black powder, resembling the mineral called molybdæna, and when distilled with nitric acid, afforded a citron-coloured oxyde.

B. A quantity of distilled water was boiled on the residuum of the first sublimation, by which a part was dissolved, and communicated a blue colour to the water.

1. Prussiate of pot-ash added to some of this blue liquor, produced a precipitate of Prussian blue.

2. Sulphuric acid added to another portion deepened the blue colour.

3. Lixivium of carbonate of soda precipitated some ochry matter.

4. And nitrate of silver was decomposed, and muriate of silver was precipitated.

* M. SAGE has observed, that molybdæna with muriate of ammoniac affords a blue sublimate. *Journ. de Physique*, 1788, p. 389.

C. Nitric acid diluted with six parts of water was then poured on the undissolved powder, and was digested on it in a sand heat.

The powder was nearly dissolved, and the solution was colourless.

1. From this solution I precipitated sulphate of lead by the means of sulphuric acid.

2. With prussiate of pot-ash I obtained a brown precipitate of molybdæna, and

3. Muriate of tin turned another portion of it blue.

From these experiments it appears that the first solution contained iron, with some molybdic acid dissolved in muriatic acid; and the second solution contained molybdic acid and lead.

Molybdate of Lead sublimed with Muriate of Ammoniac.

EXPERIMENT II.

125 Grains of the ore were mixed with two ounces of muriate of ammoniac, and put into an earthen matrass, to which a head of stone-ware was fitted. The matrass was then exposed to a sufficient degree of heat, and when all was sublimed the vessels were separated.

The black powder which remained was mixed with two ounces of muriate of ammoniac, and again sublimed.

This operation was repeated three times, after which nothing remained in the matrass. The sublimate, as before, was yellow, green, and blue.

A. Distilled water was poured on the sublimate, so as to

dissolve all of the saline part; but as the solution was turbid, it was poured on a filter, which collected a precipitate of a pale bluish-grey colour.

B. This precipitate after it had beenedulcorated was boiled with distilled water, which was afterwards filtrated.

1. Prussiate of pot-ash precipitated some iron.

2. Muriatic acid was added to another portion, after which the prussiate produced a brown precipitate of molybdæna.

3. Muriate of silver was precipitated when nitrate of silver was dropped in.

C. I then boiled lixivium of carbonate of pot-ash on the undissolved part of the residuum, by which the greatest part was dissolved. The alkali was then saturated with muriatic acid, and prussiate of pot-ash being added, precipitated some molybdæna.

On the small portion of the residuum which remained I poured diluted nitric acid. The solution was then filtrated, and I obtained a small quantity of sulphate of lead by the means of sulphuric acid.

These experiments shew that the residuum was composed of molybdic acid, iron, lead, and a small quantity of muriatic acid, which was produced from the muriate of ammoniac during the sublimation.

D. I now took the solution A and divided it into two portions, to one of which I added three ounces of concentrated sulphuric acid, and evaporated the liquor to half of the quantity.

When it was cold it deposited a white saline matter, which for the greater part dissolved in water, leaving a small residuum which appeared to be muriate of lead.

Pot-ash expelled some ammoniac from a portion of the dry salt.

And a precipitate was produced when muriate of barytes was added to the solution. This white saline matter was therefore a mixture of sulphate of ammoniac with a small portion of muriate of lead.

The solution to which the sulphuric acid had been added was again evaporated to a considerable degree, and when cold it resembled a very thick mucilage of a pale yellow colour. It readily dissolved in water, and contained sulphuric acid in great excess.

1. Prussiate of pot-ash only changed the colour to pale green.

2. Carbonate of pot-ash expelled the ammoniac, and a white precipitate like starch was formed, which was principally composed of molybdic acid and pot-ash, on which I shall not make at present any observations, as it will be hereafter noticed in several parts of this paper.

It is worthy of notice, that prussiate of pot-ash did not precipitate the molybdæna from this mucilaginous salt, and that when the pot-ash expelled the ammoniac it formed with the molybdic acid a salt more difficultly soluble than that formed by ammoniac.

E. To the second portion of the solution I added three ounces of concentrated nitric acid, and evaporated it nearly to dryness.

A bright yellow matter was deposited, which I found to be molybdic acid combined with a portion of lead.

There was also a small quantity of liquid, which I diluted with distilled water, and then precipitated some sulphate of lead by sulphuric acid. When this was separated I added

prussiate of pot-ash, and obtained a quantity of Prussian blue.

§ VIII. *Molybdate of Lead, with black Flux.*

One hundred grains of the ore were mixed with four times the weight of black flux. The mixture was then put into a crucible with a piece of charcoal over it; a cover was fitted to the crucible, and it was placed in a furnace in which a strong heat was kept up during an hour. When the crucible was cold and was broken, there did not appear any reguline button, but shining metallic particles were dispersed throughout the mass.

It was then reduced to powder, and the largest particles were separated by washing, were dried upon paper, and weighed 31 grains; upon examination they proved to be lead in the metallic state.

Other particles were separated by a magnet, and the remainder consisted of a black powder.*

A. Diluted nitric acid was poured on this black powder and dissolved it, excepting a small residuum, which consisted of siliceous earth with a little charcoal.

1. The solution was diluted with distilled water and filtrated.

2. I then first separated a quantity of lead by sulphuric

* SCHEELÉ could not reduce molybdic acid by black flux. SCHEELÉ's *Essays*, p. 238.—Several chemists however assert, that they have obtained a regulus of molybdæna, particularly Mr. HIELM, in *Journ. de Physique*, 1789, p. 372.—And Mr. RUPRECHT, *Journ. de Physique*, 1790, p. 231.—But Mr. ISLMANN did not succeed. *Journ. de Physique*, 1788, p. 296.

acid, and afterwards obtained some Prussian blue by prussiate of pot-ash.

B. The alkaline solution which had been formed when the melted mass was washed, was poured on a filter, and distilled water was added till it came away tasteless.

The filtrated liquor was without colour: nitric acid was then added till the alkali was saturated.

When about half of the requisite quantity of nitric acid was poured in, the liquor became pale blue, and as the quantity was increased it changed to green; and, lastly, when the nitric acid was added till it was in a small excess, the liquor was of a bright amber colour.

1. This solution, with prussiate of pot-ash, afforded a brown precipitate of molybdæna.

2. Muriate of tin changed the colour to a beautiful deep blue.

3. But sulphuric acid had not any effect.

C. The amber-coloured solution was evaporated to dryness, and a saline mass of a bright citron colour remained at the bottom of the vessel.

As part of the yellow colouring matter appeared to be only mixed with the salt, I dissolved it in distilled water, and separated a quantity of a citron-coloured powder, which was the molybdic acid.

The solution was twice again evaporated, and each time some molybdic acid was separated; but a part still remained intimately combined with the salt, so as with water always to produce the amber-coloured solution.*

* Although the solution at first afforded a brown precipitate with prussiate of pot-ash, yet when it had been twice evaporated, it required the addition of some nitric

I now proceeded to examine the ore with the acids.

As the results which I obtained when the ore was digested with nitric acid were the same as those mentioned by Mr. KLAPROTH, I shall not repeat them, but shall only observe, that it does not appear possible to decompose the ore completely by means of this acid.

§ IX. *Molybdate of Lead with Muriatic Acid.*

240 Grains of the purified ore in fine powder were put into a glass matrass, with three ounces of pure muriatic acid.

The matrass was then placed in a sand bath; in about an hour the whole was dissolved, excepting some muriate of lead, which I dissolved by pouring water on it.

After this there only remained a very small residuum of siliceous earth.

A. The solutions were then added together, and formed a liquor which was transparent, and of a greenish-yellow colour.

1. Prussiate of pot-ash produced a copious precipitate of molybdæna, in the form of a reddish-brown flocculent matter.

B. Lixivium of carbonate of pot-ash precipitated a yellowish-white matter, and turned the liquor to a deep blue.

C. Carbonate of soda had the same effect.

D. Solution of carbonate of ammoniac produced a similar precipitate, and caused the liquor to become blue.

acid before any precipitation could be made. The cause of this was, that the first liquor contained nitric acid in excess, which was afterwards expelled by the subsequent evaporations.

These precipitates were separately collected and washed on filters.

When examined by the blow-pipe, all of them afforded a yellowish-green glass, with phosphate of ammoniac and soda.

These precipitates dissolved in diluted nitric acid with effervescence, and sulphuric acid precipitated sulphate of lead, after which Prussian blue was precipitated by prussiate of pot-ash, and the liquor became brown.

E. The blue solution, which consisted of the muriatic and molybdic acids combined with soda, was evaporated.

When the liquor became hot, the colour changed from blue to pale yellow, and the evaporation was continued without any other perceptible alteration till the whole was become a dry concrete salt.

I dissolved this salt in distilled water, and added muriatic acid, so as to be in a small excess. The liquor was then evaporated to half, and was set in a cool place.

The following morning I found a quantity of crystallized muriate of soda at the bottom of the bason, covered with a white flocculent precipitate, which I collected andedulcorated on a filter. The rest of the liquor was repeatedly evaporated, till I had separated the greatest part of this white matter from the muriate of soda.

The last portion of the liquor, however, still contained some molybdic acid, combined with the muriate of soda; for after it had been several times evaporated and again dissolved, it became blue when muriate of tin was added; or if muriatic acid was first poured in, prussiate of pot-ash produced a reddish-brown precipitate of molybdæna.

Experiments on the White Precipitate.

1. It was not dissolved when water was boiled on it.
2. When digested with sulphuric or muriatic acid, the greatest part was dissolved, and prussiate of pot-ash produced a precipitate of a greenish-brown colour.
3. A small part became yellow when nitric acid was distilled from it.
4. The solutions of carbonate of pot-ash, soda, and ammoniac, dissolved the greater part; and when these solutions were saturated with muriatic acid, prussiate of pot-ash produced precipitates like those of the acid solutions.

As this precipitate in a great measure resembles that which is described in § X. I shall, when I come to that part, give a more ample account of it.

F. I next examined the blue solution, which consisted of the muriatic and molybdic acids combined with ammoniac.

It was first filtrated, and then gradually evaporated. When evaporated to half of the original quantity, the colour was green, but towards the end of the operation it again became blue, and when evaporated to dryness, the residuum was a whitish salt, tinged in some parts with blue.

G. This salt was reduced to powder, and was put into a small glass retort, to which a receiver was fitted. I then placed the retort in a small open furnace, and gradually raised the fire till the bottom of it began to melt. The retort was now removed, and I examined the contents. The receiver contained some water, and a small quantity of muriatic acid.

Near the extremity of the beak of the retort was some muriate of ammoniac, with some fuming muriatic acid, and the

remainder of the tube was filled with a hard greyish-blue salt. In the retort was a black pulverulent residuum.

I collected all of the blue salt, and again sublimed it, and again obtained muriatic acid, blue salt, and some of the black powder.

The blue salt was composed of muriate of ammoniac combined with the acid, or rather with a blue oxyde of molybdæna.

H. The black residuum was put into a glass retort, and some nitric acid being poured on it, it was exposed to a moderate heat. Nitrous fumes were discharged, and when the distillation had been repeated, I found the whole of this black powder converted into the citron-coloured molybdic acid.

I had evident proof that in this experiment a portion of the muriate of ammoniac was decomposed by each sublimation, and also that part of the molybdic acid was deprived of oxygen, and remained in the retort, if not in the state of metal, at least combined with so small a quantity of oxygen as to be nearly approaching to it.*

Molybdate of Lead with Muriatic Acid.

EXPERIMENT II.

One drachm of the ore was digested with muriatic acid, and distilled water was added till the whole was dissolved, excepting a small residuum of siliceous earth.

The solution was filtrated, and was repeatedly evaporated, till muriate of lead was no longer separated.

* A black powder of a similar nature appears to have been obtained by SCHEELÉ, when he distilled the white molybdic acid with a small quantity of olive oil. *Essays*, p. 238.

The muriate of lead, whenedulcorated, I found to be perfectly free from any other substance.

I now saturated the acid solution (from which the muriate of lead had been separated) with solution of carbonate of ammoniac, and obtained a pale yellow flocculent precipitate, which was welledulcorated.

This precipitate immediately dissolved in very dilute nitric acid, and with sulphuric acid I precipitated a small portion of lead, after which, with prussiate of pot-ash, I separated a quantity of iron.

The solution, when saturated with the ammoniac, was deep blue, and was composed of muriatic acid, ammoniac, and the blue oxyde of molybdæna, like that mentioned in the former experiment.

In the course of these experiments, I have observed that the full blue colour only takes place at the precise moment of saturation, and if the alkali is even added to a considerable excess, the colour does not suffer any farther change; but if much water is first added, the blue colour does not appear; or if water is added afterwards, the solution becomes colourless.

By the preceding experiments the component parts of the ore are proved to be lead, iron, and molybdic acid.

In respect to the small portion of siliceous earth, it may rather be regarded as accidentally present, than as an essential ingredient.

My second object was to discover the least exceptionable mode of analysis, but all of those which have been described appeared to me to be liable to considerable objections, and I was therefore induced to make some additional experiments.

§ X. *Molybdate of Lead with Sulphuric Acid.*

From the experiments of Mr. KLAPROTH it appears, that he only employed nitric and muriatic acid; and on this account I was desirous to try the effects of sulphuric acid, especially as SCHEELE has proved that it is able to dissolve a considerable quantity of the acid of molybdæna.* Moreover, I conceived hopes of success, on the supposition that the elective attraction between lead and sulphuric acid was more powerful than that between lead and molybdic acid; and as sulphate of lead is nearly insoluble, I should thus be able to make a complete separation of the constituent parts of the ore, I therefore made the following experiment.

120 Grains of the purified ore in fine powder were put into a small glass matrass, and one ounce of concentrated sulphuric acid was poured on the powder.

The matrass was then placed over an ARGAND lamp, and the acid was boiled during an hour. The ore became white, and the acid was of a beautiful blue.

When it had stood some hours, I poured the acid into another vessel,edulcorated the powder with distilled water, and added the washings to the acid solution.

Another ounce of sulphuric acid was poured on the powder, and boiled as before. It was faintly tinged with blue; and I added it to the first solution, as well as the water with which the powder was washed.

That I might not leave any part of the molybdic acid unextracted, I repeated the operation a third time. The powder

* *Essays*, p. 235.

was thenedulcorated, and the acid solutions being added together, formed a pale blue transparent liquid.

To decompose the white residuum, I boiled it during an hour with lixivium of carbonate of soda, then washed the powder, and poured on it nitric acid much diluted, by which it was immediately dissolved with effervescence, leaving a very small residuum of siliceous earth.

Prussiate of pot-ash produced a white precipitate of lead, and after 12 hours, a very small portion of Prussian blue subsided.

The ore was therefore decomposed, and there only remained this minute portion of iron to be separated from the lead; but this I shall notice when I come to the analysis.

I now diluted the sulphuric solution with a large quantity of distilled water, and divided it into two portions.

One of these (which I shall call A) was saturated with carbonate of pot-ash. The other (B) was saturated with carbonate of ammoniac.

When the alkalies were first added, the solutions became of a pale yellowish green, and as the quantity of the alkalies was increased, the solutions changed to bluish green, and lastly to deep blue.

When the vessels had stood about 24 hours, the solution A deposited a white precipitate, and in the solution B there was also a small quantity of a yellowish colour.

Both solutions passed the filter without any diminution of the blue colour.

I collected the white precipitate of A on a filter, and then evaporated the liquor to half.

The following morning I found a large quantity of crystal-

lized sulphate of pot-ash covered with a flocculent white precipitate. This I separated from the sulphate of pot-ash, and by repeated evaporations obtained the remainder.

These white precipitates were kept separate in the order in which they were obtained, and were washed and dried.

Experiments on the first Portions of the White Precipitate obtained by the Addition of the Alkali, and by the first Evaporation.

The white precipitate, when exposed on charcoal to the blow-pipe, melted into a pale green transparent globule.

With borax it formed a yellow transparent glass when hot, which as it cooled became opaque, and of an ash colour.

When added to the phosphate of ammoniac and soda in fusion, a yellowish green transparent glass was produced.

Water boiled for a considerable time on the precipitate did not apparently dissolve it; but muriate of barytes shewed the presence of a small quantity of sulphuric acid.

Nitric acid distilled to dryness from some of the precipitate, produced very little alteration, excepting that a small part became yellow.

Sulphuric acid was digested on a portion of the precipitate, and dissolved part of it; the remainder appeared unchanged.

The solution was diluted with distilled water, and prussiate of pot-ash being added, produced a blue precipitate.

Muriatic acid digested on another portion, turned it at first yellow, but afterwards the greater part became white, and remained undissolved.

The solution afforded a blue precipitate with prussiate of

pot-ash, and a small quantity of white precipitate with muriate of barytes.

The residuum was not affected when afterwards digested with acids or alkalies.

Some of the white precipitate was boiled with lixivium of carbonate of pot-ash, and part was dissolved. The solution was then saturated with muriatic acid, and prussiate of pot-ash produced a blue precipitate.

With carbonate of soda the effects were the same.

A solution made with carbonate of ammoniac (afterwards saturated with muriatic acid) was tinged green by the addition of prussiate of pot-ash.

A mixture, composed of 20 grains of the precipitate, and 50 grains of sulphur, was put into a small glass retort, and distilled till all of the sulphur was driven over.

The powder in the retort was of a pale grey colour, did not stain the fingers, or feel greasy, and had an hepatic smell.

Diluted nitric acid was digested on it without heat, and when prussiate of pot-ash was added to a part of the clear solution, a brown cloud was produced in about 10 minutes, resembling the usual precipitate of molybdæna.

Lixivium of carbonate of pot-ash added to another portion, formed a white flocculent precipitate, like starch.

Concentrated nitric acid was afterwards digested on the grey powder in a strong heat, and dissolved a considerable part.

With this solution, prussiate of pot-ash produced a brown precipitate, intermixed with some blue particles.

The rest of the solution was then evaporated, and left a bright yellow mass at the bottom of the matrass.

The undissolved residuum of the nitric solution was then boiled with lixivium of pot-ash, which was afterwards saturated with muriatic acid, and became tinged with blue when prussiate of pot-ash was added.

The residuum was now a black powder, which was edulcorated, and was immediately dissolved when nitric acid was poured on it; at the same time nitrous fumes were emitted. The solution was transparent, excepting that a few white particles were floating in it.

It was then diluted, and filtrated.

Prussiate of pot-ash turned it to a brownish-green, which afterwards became brown. Lixivium of pot-ash precipitated a white flocculent matter; and caustic ammoniac, added to a third portion, precipitated a quantity of iron.

As this precipitate had some remarkable properties, particularly in respect to the difficulty with which it was decomposed, I have been induced to mention the experiments made on it in a circumstantial manner.

This precipitate appears from these experiments to be principally composed of iron, and some molybdic acid, together with a small portion of alkali and sulphuric acid.

The intimate union between the iron and molybdic acid is apparently the cause which impedes the decomposition of this precipitate; but this can only be ascertained by future experiments on molybdate of iron.

I next examined the white precipitate which was deposited by the last evaporations, and found that (when distilled with nitric acid) it was converted into the yellow molybdic acid; and I was therefore convinced that this last portion of the

white precipitate was the same neutral salt which I obtained in several other operations, and which has also been noticed by SCHEELE and KLAPROTH.*

I now began to examine the blue solution B, which consisted of the sulphuric solution of molybdic acid, saturated with ammoniac ; but that the experiments made on this may be better understood, I shall first give an account of some experiments and observations which I have made on the sulphate of ammoniac.

Experiments and Observations on the Sulphate of Ammoniac.

This neutral salt, which from GLAUBER (who first prepared it) was called the secret ammoniacal salt of GLAUBER, or vitriolic ammoniac, has been very little examined ; neither has it been applied to any useful purpose, although the inventor much recommended it in metallurgical operations.

It has been long known that the fixed alkalies, lime, and barytes (when triturated with it), decompose it, by uniting with the acid. But the effects of heat on it do not appear to have been sufficiently observed.

MACQUER says, that it is (to use his expression) demi-volatile, that it may be sublimed entire, and that it cannot be decomposed in close vessels without some intermediate substance.†

BAUME' makes use of nearly the same expressions.‡

* SCHEELE observes, when molybdæna was detonated with nitre, and the mass afterwards dissolved in water, and saturated with sulphuric, nitric, or muriatic acid, that a white precipitate was produced, which was the acid of molybdæna combined with a portion of alkali. *Essays*, p. 231, and 240.

† *Dictionnaire de Chimie*, Tom. I. p. 111.

‡ *Chimie Expérimentale et Raisonnée*, Tom. II. p. 83.

BUCQUET says, that when it has lost the water of crystallization, it becomes red hot, and melts without being volatilized.

Lastly, M. FOURCROY mentions it in the following manner: "As it contains much water of crystallization, it immediately liquefies by a very moderate heat; but by degrees it becomes dry, in proportion as the water of crystallization is dissipated. In this state it first becomes red hot, and soon melts without being volatilized, according to BUCQUET; but M. BAUME' asserts that it is demi-volatile. In repeating this experiment I have observed, that in fact a part of this salt is sublimed, but a *portion remains fixed in the vessel*, and without doubt it is concerning this that BUCQUET speaks."*

When so many eminent chemists concurred in nearly the same assertion, I was not a little surprised to observe, in some experiments (which I made for a very different purpose), that the whole of the sulphate of ammoniac was not only volatilized by heat, but also that the distillation of it was accompanied with some remarkable phænomena.

I therefore diluted some very pure concentrated sulphuric acid with an equal quantity of distilled water, and having saturated it with ammoniac, I gradually evaporated it till it became a concrete salt.

EXPERIMENT I.

I put two ounces of the salt into a glass retort, capable of containing three times the quantity, then fitted on a receiver without any luting, and placed the retort in a small open furnace over some lighted charcoal.

The salt in the retort speedily liquefied, and a small portion

* *Elémens d'Histoire Naturelle et de Chimie*, Tom. II. p. 93.

of water first came over ; this was succeeded by a considerable quantity of alkaline gas, which continued to be produced during 15 or 20 minutes. On a sudden the vessels were filled with a thick white cloud, which upon close inspection appeared to be composed of very minute glittering crystals. This cloud quickly disappeared, and was followed by a great quantity of sulphureous gas and water, the greatest part of which was condensed in the receiver ; and the operation went on in this manner while any thing remained in the retort.

During the distillation, the matter in the retort was always liquid ; and when the operation was finished, I found in the receiver a considerable quantity of sulphureous acid, with some ammoniac in solution ; and in the neck of the retort there was sublimed a portion of the undecomposed salt.

From this experiment I was in a great measure convinced, not only that the neutral salt was decomposed, but that the ammoniac was also in part resolved into its constituent principles.

EXPERIMENT II.

That I might, however, remove any doubt respecting this matter, I fitted a bent glass adopter to a retort, and to this added a double tubulated receiver, from which proceeded a bent tube, which passed under a glass jar filled with water and inverted.

The former experiment was now repeated with this apparatus ; and I had the satisfaction to observe, that when the sulphureous acid began to be produced, a quantity of gas at the same time displaced the water in the jar, and continued to pass into it to the end of the operation.

This gas I afterwards examined, and found that it possessed all the properties of the azotic gas.*

I afterwards distilled 100 grains of the yellow oxyde of iron, mixed with 200 grains of sulphate of ammoniac.

Pure ammoniac first came over, and afterwards some sulphureous acid. When the retort began to melt I removed it, and found the iron chiefly in the state of the red oxyde, or colcothar, mixed with some sulphate of iron.

When oxyde of zinc was used, the residuum was sulphate of zinc.

Minium, when triturated with sulphate of ammoniac, immediately decomposed it like lime, or the alkalies, and when distilled, the retort contained sulphate of lead.

When native green oxyde of copper was distilled with sulphate of ammoniac, the residuum was partly red oxyde of copper, with some sulphate of the same. But the ammoniac came over in a concrete state, by reason of the carbonic acid contained in the green oxyde.

The oxydes therefore of iron, zinc, lead, and copper decompose the sulphate of ammoniac by combining with the acid.

I next mixed it with the yellow tungstic acid; but after the distillation, I found the tungstic acid unchanged, excepting that it had acquired a tinge of pale green. The ammoniac

* This operation requires to be conducted with caution; for at the moment when the white cloud appears, a vacuum takes place, occasioned by the alkaline gas (which previously filled the vessels) being neutralized by the sulphureous gas, which is then produced. It is necessary, therefore, in about 10 or 15 minutes after the commencement of the operation, that the fire should be raised, and the azotic gas will then soon begin to pass into the jar. Some water will most commonly rush into the receiver, but if the capacity of this is not too small, there will not be time enough for the water to rise sufficiently high, so as to pass into the retort.

and the sulphureous acid also came over in the same manner as when only the sulphate of ammoniac was distilled.

Lastly, I distilled one ounce of the sulphate of ammoniac with 20 grains of the yellow molybdic acid. During the distillation, the ammoniac and sulphureous acid were produced in as great quantities as when the sulphate of ammoniac was distilled by itself. But the molybdic acid remained in the retort, deprived of oxygen, in the form of a black blistered matter, which was again converted into the yellow acid when distilled with nitric acid.

From these experiments it appears, that the sulphate of ammoniac is not (as many eminent chemists have imagined) incapable of being decomposed without some intermediate substance, but on the contrary, the whole of it can be raised, and a great part decomposed, whenever a proper degree of heat is applied; for then a certain portion of ammoniac first comes over, so that the remainder is combined with acid in excess, and the hydrogen of the ammoniac which remains unites with part of the oxygen of the sulphuric acid, and forms water, which passes into the receiver, accompanied by the acid (now become sulphureous acid), and by the azote in the state of gas.

Various methods have long been in use to decompose ammoniac.

Metallic oxydes produce this effect; and SCHEELÉ particularly mentions, that if arseniate of ammoniac is distilled, gas is produced, and the acid of arsenic is reduced to the metallic form, and as such is sublimed.*

* *Essays*, page 155. The same effects also were produced when acid of arsenic was sublimed with muriate of ammoniac, page 161.

The decomposition of the nitrate of ammoniac is also well known; and I have no doubt but that muriate of ammoniac suffers a similar decomposition in a smaller degree each time that it is sublimed; for whenever I have had occasion to sublime muriate of ammoniac, I have always found some fuming muriatic acid; and from whence could this be produced, but from a portion of the salt which was decomposed during the sublimation.

The distillation of the blue triple salt, composed of molybdic acid, muriatic acid, and ammoniac (§ VII. and IX.), places this in a stronger light; for whenever this salt was distilled, a certain portion of molybdæna was left in the retort deprived of oxygen, and muriatic acid was found in the receiver. Moreover, from several repetitions of this experiment, I am well convinced, that by a great number of sublimations the whole of the molybdæna might have been obtained in the proportion that the muriate of ammoniac was decomposed.

When all these facts are considered, it appears to me more than probable that most, if not all, of the ammoniacal salts suffer different degrees of decomposition whenever they are treated in the dry way.

As the molybdic acid was my principal object, I did not make all the experiments I could have wished on this neutral salt; neither have I as yet exactly determined the proportion of azotic gas produced from a certain quantity.

I have found, however, that the sublimed undecomposed part of the salt amounted to 183 grains when an ounce of the salt had been distilled, and that the liquid in the receiver weighed 145 grains; so that 152 grains had escaped, which

principally consisted of azotic gas, together with some sulphureous acid, and some alkaline gas, which had made their way out of the vessels during the operation.

Continuation of the Experiments on the Molybdate of Lead.

From the effects which I observed to be produced when sulphate of ammoniac was distilled with molybdic acid, I was induced to examine in a similar manner the blue solution B; but first I collected, washed, and dried the pale yellow precipitate which had been formed when the sulphuric solution of the molybdic acid was saturated with ammoniac.*

This precipitate, when dry, appeared of a deeper yellow, and easily dissolved in muriatic acid.

Prussiate of pot-ash was then added to the clear solution, and precipitated the whole of the dissolved matter in the state of Prussian blue.

The filtrated solution B was now evaporated till it became a dry concrete salt, the colour of which was pale greyish blue.

I collected this salt, and having reduced it to powder, put it into a small glass retort, and having fitted on a receiver, I distilled it in the same manner as was employed with the sulphate of ammoniac.

The products which came over were also the same, and when the bottom of the retort began to be softened by the

* Whenever the solution was sufficiently diluted, I always found that ammoniac precipitated the iron free from any part of the molybdic acid; but if either of the fixed alkalies were used, a portion of molybdic acid was precipitated with the iron in a state similar to the first portions of those white flocculent precipitates, which have been already mentioned in § IX. and § X.

heat, I removed it, and found the residuum to be a black blistered matter.

I then examined the sulphureous acid and sulphate of ammoniac which had risen, but did not find any trace of molybdæna.

I next poured nitric acid diluted with an equal weight of distilled water on the black residuum in the retort, and distilled it.

As soon as the acid began to be warm, nitrous fumes were discharged, and when the distillation had been repeated with a second portion of nitric acid, I found the whole of the black matter converted into a pale citron-coloured substance, which was the molybdic acid.

I shall not here mention the experiments made on this acid, but shall speak of them after I have given an account of the analysis of the molybdate of lead, which I immediately attempted, according to the method pointed out by the foregoing experiments.

§ XI. *Analysis of the Molybdate of Lead.*

I put 250 grains of the purified ore reduced to a fine powder into a glass matrass, and having poured on it one ounce of concentrated sulphuric acid, I digested it in a strong heat during an hour.

When the solution was become cool and had settled, the acid was cautiously decanted from the powder, and distilled water was poured on till it came away tasteless.

The same operation was repeated twice, so that three ounces of sulphuric acid were used.

The acid solutions and washings were then filtrated, and were received in a large glass vessel.

I diluted the pale blue liquor with distilled water, in the proportion of sixteen to one, and afterwards gradually added ammoniac, until it was completely saturated. The liquor then became deep blue, and appeared turbid.

When it had stood about 24 hours, a loose pale ochry precipitate subsided, and was collected on a filter, the weight of which had been noted.*

This precipitate wasedulcorated, and afterwards dried with the filter on the flat top of a tin vessel heated by boiling water, after which the weight of the precipitate was 4.2 grains.

The colour of the dry precipitate was yellowish brown, and when dissolved in muriatic acid it was precipitated by prussiate of pot-ash in the state of Prussian blue.

I now poured part of the clear blue solution, which was composed of sulphuric and molybdic acid saturated with ammoniac, into a glass retort, and when about half was evaporated, I continued to add the remainder of the liquor at different times till the whole was become a concrete salt.

I then raised the fire and continued the distillation until all of the sulphate of ammoniac was decomposed or driven over ; but as some of the sublimed salt was fixed in the neck of the

* This is one of the many instances which prove the weak affinity between molybdæna and oxygen ; for it is well known that pure ammoniac precipitates iron from sulphuric acid, in a state nearly similar to martial ethiops ; but in the present case the iron takes a considerable portion of oxygen from the molybdic acid at the moment that the acid menstruum is saturated by the ammoniac, and it is therefore precipitated in the form of a yellowish-brown oxyde, whilst the molybdic acid being thus deprived of so large a quantity of oxygen, is converted into a blue oxyde which remains in solution.

retort, I turned the bottom of it upwards, and poured some distilled water into the neck, so as to wash out the salt; after this I increased the fire until the whole body of the retort was become red hot.*

The residuum in the retort was a black blistered mass, upon which I poured three ounces of nitric acid diluted with an equal portion of water, and having distilled it, I repeated the operation, and thus converted the whole of the black matter into the yellow acid of molybdæna.

When the retort was sufficiently cooled, I cut off the neck and removed the powder, which weighed 95 grains.

I next proceeded to decompose the residuum left by the acid solution in the state of sulphate of lead, and havingedulcorated it, I boiled it during an hour with four ounces of lixivium of carbonate of soda, then washed the powder, and poured on it nitric acid much diluted.

The whole was dissolved, excepting a small portion of white powder, which was washed and dried on a filter by the heat of boiling water, and then weighed seven-tenths of a grain.

This, upon examination, proved to be siliceous earth.

I then exactly saturated the nitric solution with lixivium of pure or caustic soda, and having washed and dried the precipitate of lead, I exposed it in a porcelain crucible for a quarter of an hour to an heat rather below red; after which it weighed 146 grains.

As I had found by a former experiment that a small portion of iron remained with the lead, I dissolved the 146 grains in diluted nitric acid, and precipitated the lead by sulphuric acid.

* To be certain that all of the ammoniacal salt is decomposed, it is absolutely necessary that the retort should be made red hot.

The solution was then filtrated, and being saturated with pure ammoniac, I obtained a small quantity of oxyde of iron, which, when dried as before, weighed one grain.

By this analysis, 250 grains of the ore yielded

| | | | Grains. |
|------------------------|---|-----|------------|
| oxyde of lead | — | — | 146 |
| molybdic acid | — | — | 95 |
| oxyde of iron | { | 4 2 | — 5 2 |
| | 1 | } | |
| and siliceous earth | — | — | 0 7 |
| | | | grs. 246 9 |
| the loss was therefore | — | — | 3 1 |
| | | | 250 0 |

which I am inclined to place principally to the account of the lead, as it is scarcely possible to decompose the sulphate of lead without some loss, occasioned by the action of the alkaline solution.

§ XII. *Experiments on the yellow Molybdic Acid, obtained by the Analysis.*

A. When exposed to the blow-pipe on charcoal, it was melted by the exterior flame, and the sides of the charcoal were covered with small long crystals, which had a metallic lustre resembling silver.*

When the heat was continued the whole was melted, and

* SCHEELE mentions a similar product obtained when molybdæna was exposed to the blow-pipe. Essays, p. 230.—Also by sublimation. Essays, p. 238.—And *Mémoire sur la Molybdène, par M. PELLETIER. Journ. de Physique, Decembre, 1785, p. 439.*

for the greater part absorbed by the charcoal, the edges of which became covered with a blue powder.

When melted in a spoon of platina, some yellow powder was deposited near the edges, and a brownish-yellow shining matter was formed, which became streaked in cooling.

With borax it produced a brownish-yellow glass, but if the quantity of molybdic acid was small, the colour was sometimes blue when the globule was heated by the interior flame.

With soda in the platina spoon it formed a brownish opaque matter.

And with phosphate of ammoniac and soda it formed a glass, which (in proportion to the quantity of molybdic acid) varied from a greenish blue to a deep blue.

B. Ten grains of the yellow molybdic acid were boiled with six ounces of distilled water. About three grains were dissolved, and the solution when filtrated was of a pale yellow colour.

It had scarcely any perceptible flavour, but turned litmus paper red.

When prussiate of pot-ash was added to a portion of the solution, no apparent change was effected; I therefore added a small quantity of nitric acid, which produced a copious brown precipitate of molybdæna. The sulphuric and muriatic acids had the same effect, when poured into the solution, either before or after the addition of prussiate of pot-ash.

With muriate of tin it changed to a beautiful deep blue.

Lead was precipitated from solution of nitrate of lead, in the form of a pale yellow precipitate, which was a regenerated molybdate of lead.

Nitrate of barytes rendered the solution slightly turbid, but

I did not find that the precipitate which subsided was soluble in cold water, as SCHEELE has mentioned.*

The solution did not precipitate lime from nitric acid.

C. Ten grains of the yellow molybdic acid were dissolved when digested with an ounce of concentrated sulphuric acid.

The solution as it cooled became blue.†

Prussiate of pot-ash produced a reddish-brown precipitate.

Muriate of tin had not any effect.

When a portion of the solution was distilled to dryness, the yellow molybdic acid was left in its original state.‡

The remainder of the solution was saturated with lixivium of soda, by which the blue colour was heightened, and some white flocculent matter was precipitated.

Prussiate of pot-ash added to part of this saturated solution did not precipitate the molybdæna, until the alkali was again supersaturated with an acid.

Muriate of tin poured into the solution saturated with alkali changed it to a deep blue; but when the alkali was again saturated with an acid the muriate of tin ceased to have any effect.

The white flocculent matter which was precipitated when

* Essays, p. 234.—SCHEELE does not mention the quantity of water which he employed.

† SCHEELE observes that sulphuric acid dissolves a considerable quantity of molybdic acid, and that the solution as it cools becomes blue and thick; but when heated, the colour disappears, and returns again as the liquor grows cold. Essays, p. 235.

‡ M. PELLETIER says, that a small portion of molybdæna is raised by sulphuric acid when distilled with it; but I did not find it so with the molybdic acid.—*Mém. sur la Molybdène, Journ. de Physique, Decembre, 1785.*

the solution was saturated with soda, wasedulcorated and heated with nitric acid, by which it was converted into a yellow powder, similar to the molybdic acid which had been dissolved.

D. Ten grains of the yellow molybdic acid, when digested in a strong heat with one ounce of concentrated muriatic acid, formed a pale yellowish-green solution.

Prussiate of pot-ash precipitated the molybdæna.

Muriate of tin had not any effect.

A portion of the solution being distilled to dryness, left a greyish-blue residuum.*

I then saturated the remaining part of the solution with lixivium of pot-ash, by which the blue colour became more apparent, and a much larger quantity of white flocculent matter was precipitated than when soda was employed.

Prussiate of pot-ash did not affect this solution, until the alkali was again saturated with an acid.

Muriate of tin was precipitated by the solution saturated with alkali, highly coloured with blue; but when the alkali was again saturated with an acid, the muriate of tin had not any effect.†

* SCHERLE has made the same observation. *Essays*, p. 235.

† From the effects produced by muriate of tin on the molybdic acid dissolved in water, in acids, and in alkalies, it appears that it always tends to deprive the molybdic acid of a great part of its oxygen; and when water is the menstruum, the muriate of tin does this effectually; but when the molybdic acid is dissolved in sulphuric or muriatic acid, the muriate of tin has not any effect, because (as I conceive) the oxygen is supplied by the acid menstruum. This seems the more evident from the effects produced by the muriate of tin when the excess of acid is saturated by an alkali.

Lastly, the white flocculent matter was boiled with nitric acid, and became like the molybdic acid before it was dissolved.

E. Nitric acid did not appear to have any effect on the molybdic acid when digested with it.

F. Two ounces of lixivium of carbonate of pot-ash were poured on ten grains of the molybdic acid.

In a few minutes, carbonic acid was gradually expelled, and as the molybdic acid dissolved, a white flocculent matter was deposited.

After it had stood some hours, the clear liquor was decanted from the residuum.

Prussiate of pot-ash did not affect this solution. Some nitric acid was then dropped in, and produced a reddish-brown precipitate, which was redissolved until the acid was in some excess.

Muriate of tin, when added to a portion of the alkaline solution, was precipitated white, but when some muriatic acid was dropped in, the precipitate became blue.

The white flocculent residuum, when treated with nitric acid as in the former experiments, was converted into the yellow molybdic acid.

Another portion of the alkaline solution was evaporated to one-fourth, and in proportion as the evaporation advanced, some of the white flocculent matter was precipitated, but I did not obtain any crystals.

G. Two ounces of lixivium of carbonate of soda were poured on ten grains of molybdic acid.

In a few minutes carbonic acid was expelled, and when the

molybdic acid was dissolved, a small quantity of white flocculent matter was precipitated.

The clear solution was then poured from the residuum.

Prussiate of pot-ash did not produce any precipitate until the alkali was saturated with an acid.

The effects of muriate of tin were also the same as those mentioned in the former experiment.

A part of the solution was evaporated to half, and the next morning I found crystals, which although not very distinct, appeared to be in the form of four-sided tables with the angles truncated.

These crystals dissolved in water without leaving any residuum, and (when the solution was saturated with muriatic acid) the molybdic acid was precipitated by prussiate of pot-ash, as in the former experiments.

H. Two ounces of carbonate of ammoniac in solution were poured on ten grains of molybdic acid, which appeared to be more readily dissolved than when the fixed alkalies were employed.

The solution appeared slightly turbid, but very little of it was precipitated.

The effects produced by prussiate of pot-ash and muriate of tin were the same as in the preceding experiments.

When a portion of the solution was distilled to dryness, part of the molybdic acid remained unchanged, but another part was deprived of oxygen, and appeared in the form of a dark grey powder.*

The remaining part of the solution was considerably eva-

* SCHEELÉ has observed a similar effect.

porated; and the following day I found a striated yellowish mass, which dissolved in water without leaving any residuum. This solution resembled the former in every respect.

§ XIII. *Molybdic Acid with Sulphur.*

In order to remove every doubt concerning the nature of the yellow acid obtained by the analysis, I made the following experiment.

I put 20 grains of the yellow acid and 100 grains of sulphur into a small glass retort, and continued the distillation till the bottom began to melt.

The residuum was a black substance, which was greasy to the touch, stained the fingers black, communicated to them a shining metallic lustre, and had all the other properties of the mineral known by the name of Molybdæna.

I afterwards distilled this black matter with nitric acid, which converted it into a yellow powder, similar in appearance and properties to the molybdic acid which had been originally employed.

§ XIV. *General Observations.*

It has been proved in the course of this paper that molybdate of lead can be decomposed in the humid way by the fixed alkalis, although these have not any effect when boiled with molybdæna mineralized by sulphur.* The state of the molybdæna in the two substances appears to be the cause of this

* SCHEELLE'S *Essays*, p. 230; and *Mémoire sur la Molybdène*, par M. PELLETIER. *Journal de Physique*, 1785, p. 437.

difference, for in the former it is oxygenated, but in the latter I conceive it to be in the state of metal.

From the experiments of SCHEELÉ it also appears, that of all the known acids only two have any effect on the sulphurated molybdæna, and that these two are the nitric acid, and that of arsenic. The latter, however, seems rather to act on the sulphur than on the molybdæna; but the former communicates oxygen to both, so as to convert the one into sulphuric and the other into molybdic acid.

The rapidity with which nitric acid oxygenates molybdæna, even to supersaturation, resembles the effects produced by the same acid on some other metallic substances, particularly tin; for in both cases the acid ceases to act as soon as the supersaturation with oxygen is effected; and on this account the nitric acid is unable to dissolve the molybdic acid.

Before I proceed, I must observe that whenever a solution of the molybdic acid becomes blue, or tending towards that colour, it is a certain sign that the molybdic acid has suffered a diminution of oxygen. A variety of facts which prove this, have been already brought forward in the different experiments contained in this paper; and I shall soon have occasion to mention others.

Sulphuric acid can dissolve a considerable quantity of molybdic acid; and the solution is always more or less of a blue colour according to the quantity which is dissolved; and the blue colour proves that the molybdic acid has parted with a portion of oxygen; but if the solution be heated, the blue colour disappears, and returns again when the liquor becomes cold.*

* If lead or any other metal is present, the blue colour is permanent.

The cause of this I believe to be a change produced by heat in the respective degrees of affinity which prevail between the metallic base and oxygen, and between the base of the acid menstruum and oxygen; so that when the solution is heated, the affinity between the blue oxyde of molybdæna and oxygen is increased, and a portion of oxygen therefore quits the acid menstruum and combines with the blue oxyde, which then becomes molybdic acid; but as soon as the heat is dissipated, the cause of this augmentation of affinity ceases, and the acid menstruum receives again the portion of oxygen from the molybdic acid, which then returns to the state of a blue oxyde; or if the heat is continued until the solution is distilled to dryness, the residuum is the molybdic acid exactly in the same state as it was before the solution was made, for the continuation of the heat enables it to retain the portion of oxygen requisite to constitute a metallic acid.

I do not therefore believe that the total quantity of oxygen in the solution suffers alteration any further than that it is distributed in different proportions between the two acidifiable bases, sulphur and molybdæna, according to the temperature of the solution.

As the affinity between azote and oxygen is comparatively weak, the metal molybdæna effects a decomposition of the nitric acid, and acquires a sufficiency of oxygen to become molybdic acid. But as the affinity between sulphur and oxygen is greater than that of azote, and also under certain circumstances superior to molybdæna, the latter requires the assistance of heat to be able to retain a full portion of oxygen, and this increase of affinity lasts no longer than during the continuation of the heat.

To corroborate this assertion, it will be proper to consider the effects of muriatic acid on that of molybdæna, especially as the affinity between the radical principle, or base of the muriatic acid, and oxygen is known to be so great, that no chemist has as yet been able to effect a separation of the constituent principles.

It has been mentioned, that molybdic acid when dissolved in muriatic acid also parts with some oxygen, and tinges the menstruum with a green colour. But heat does not enable it to take back the oxygen, for it augments the effects of the muriatic acid, which, when distilled, passes oxygenated into the receiver, and the molybdic acid is converted into a bluish-grey oxyde.*

These effects clearly prove, that heat in this case acts inversely to what it did when the nitric and sulphuric acids were the menstrua. For then the increase of affinity was between molybdæna and oxygen, but here it is in favour of the base of muriatic acid; so that by the continuation of heat, the muriatic acid carries with it into the receiver a certain portion of oxygen which it has taken from the molybdic acid, and the latter is left in the state of an oxyde.

From this it appears that muriatic acid uniformly tends to deprive the molybdic acid of a certain quantity of oxygen, and that heat produces a contrary effect on this solution to that which it did on the one made with sulphuric acid; and heat and cold do not therefore produce a change of colour.

I do not, however, believe that muriatic acid acts thus constantly on all of those metals which can be dissolved by it; on the contrary, there is a muriatic solution which much re-

* *Elémens d'Hist. Nat. et de Chimie, par M. de FOURCROY, Tome II. p. 439.*

sembles the sulphuric solution of molybdic acid in the vicissitudes of colour which it exhibits by heat and cold.

The phenomena which heat produces on the solution of cobalt in muriatic or nitro-muriatic acid, called sympathetic ink, have long engaged the attention of chemists and others, but as yet great difficulties have occurred whenever an explanation has been attempted.

There can be no foundation for the idea which some have had, that the green colour (which characters traced with this solution on paper assume when heated) is caused by a temporary crystallization of the salt, and the disappearance of the colour by a subsequent degree of deliquescence; because any quantity of the liquid becomes green when heated.

The effects caused by heat on the sulphuric solution of molybdic acid have therefore induced me to suspect a similar cause in the muriatic solution of cobalt; and I believe that heat and cold in like manner causes a temporary difference to take place in the proportions of oxygen existing in the acid menstruum and the oxyde; and this is the more confirmed when the acid is expelled by too great a degree of heat, for then the changes of colour are no longer to be observed.

Heat, it is well known, assists the combination of oxygen with the metals, but I do not believe that the abovementioned alternate effects of heat and cold have been as yet investigated.

It is probable that these are not confined to the two instances which have been adduced, although in other solutions they may not be so apparent. The subject is certainly curious, and worthy of the attention of chemists, as it would reflect much light on the solutions of metals in general.

When the sulphuric or muriatic solutions of the molybdic

acid are saturated with pot-ash or soda, they assume a very deep blue colour at the moment of saturation. The molybdæna is not, however, precipitated in the form of the blue oxyde, but for the greater part remains combined with the acid menstruum and the alkali, and thus forms a triple salt in solution, which differs considerably from another triple salt, which is slowly precipitated at the time of saturation in the form of a white flocculent matter, and is composed of the same three ingredients, but contains the oxyde in the largest proportion.

Sometimes a fourth ingredient becomes added to the last mentioned white precipitate ; for when iron is present in the sulphuric or muriatic solutions, it is precipitated by pot-ash or soda intimately combined with the other ingredients, and appears to render the decomposition of the precipitate very difficult.

Although the triple salt which is in solution will pass many folds of paper without leaving any residuum, yet it is not permanent ; for by repeated evaporations, the neutral salt resulting from the combination of the acid menstruum and the alkali becomes crystallized, and a white flocculent matter is separated, which does not contain iron like that which was precipitated when the acid solution was saturated with the alkali, but can be converted into the yellow molybdic acid by being distilled with nitric acid, which takes from it the small portion of the acid menstruum and the alkali required to constitute the triple salt.

It has already been observed, that nitric acid has not any effect when immediately digested on molybdic acid, but I have found it otherwise when a third substance was present ;

and the effects were nearly the same whether this substance was a metal or an alkali.

The portion of molybdic acid which I detected in the nitric acid employed to purify the ore, and Mr. KLAPROTH's experiments made with the same acid, prove the first, and the experiment mentioned in § VIII. is a proof of the latter.

The phænomena which appeared in the last experiment throw some light on the effects produced by nitric acid on molybdæna; for when the sulphuric and muriatic solutions of the molybdic acid were saturated with pot-ash or soda, they gradually changed to yellowish green, and so on to blue, in proportion as the alkali was added; but when nitric acid was added to the alkaline solution, the change of colour was exactly the reverse of the former, for the changes were then blue, green, and yellow, in proportion to the quantity of nitric acid.

The cause of these effects I conceive to be the different degrees of oxygenation of the molybdæna; for when the first portion of nitric acid was added, it rather combined with the alkali than with the molybdic acid, and the latter was therefore in some degree separated with a diminution of the original quantity of oxygen, and consequently appeared as the blue oxyde in solution. After this, the second portion of nitric acid began to oxygenate the blue oxyde, and therefore changed the colour of the solution to green; but the third addition of nitric acid acted immediately on the oxyde, turned the solution yellow, and when assisted by heat, caused a quantity of the yellow molybdic acid to be precipitated. The alkali, however, appears to have impeded the complete separation of the molybdic acid, and retained a part of it together with the nitric acid, so as to form a yellow triple salt.

When the sulphuric and muriatic solutions of the molybdic acid are saturated with ammoniac, triple salts are formed, which are different in their properties from those which have been described ; for the triple salts produced by ammoniac are permanent, and do not appear to be decomposed by evaporation.

If iron is present in the acid solution (sufficiently diluted), it is precipitated by ammoniac free from molybdic acid, especially when the menstruum is the sulphuric acid.

The affinity of the molybdic acid with muriate of ammoniac is so great, that by sublimation it even in part quits lead to unite with it, and then forms the blue triple salt, from which the blue oxyde does not separate, but in proportion that it is deprived of oxygen by the gradual decomposition of the ammoniac caused by repeated sublimations.

When the sulphuric solution saturated with ammoniac is evaporated to a proper degree, the triple salt crystallizes in the usual figure of the sulphate of ammoniac, but the colour is bluish green. If, however, the evaporation is continued to dryness, a pale greyish-blue salt is left, and by distillation this salt is decomposed (after the manner of the decomposition which I have noticed in the sulphate of ammoniac), and the molybdæna remains in the form of a black powder, deprived of oxygen.

I think it necessary here to observe, that when molybdæna is not in the metallic state, it appears to me to suffer four degrees of oxygenation. The first is the black oxyde ; the second is the blue oxyde ; the third is the green oxyde, which (as it seems to be intermediate between an oxyde and an acid) I am inclined to call molybdous acid, according to the distinction made by the new Nomenclature ; the last and fourth

degree is the yellow acid, or that which is supersaturated with oxygen.

The affinity between molybdæna and oxygen is but weak, at least in respect to that portion which is required to constitute molybdic acid; for it has been proved, in the course of these experiments, that considerable changes are produced by a very small difference in the proportions of the acids or alkalies, and even by the degrees of heat. SCHEELE and Mr. ISLMANN have observed, that all of the metals, excepting gold and platina, are able in the humid way to deprive the molybdic acid of oxygen, so as to cause it to become blue; but here their effects appear to cease. M. PELLETIER found that a solution of molybdic acid was turned blue when hydrogenous gas was passed through it. Mr. KLAPROTH has also remarked that light, under certain circumstances, changed the colour of molybdic acid to blue. And the effects of light appear in some measure to be connected with the following experiment.

I made a solution of the molybdic acid, by digesting sulphuric acid on molybdate of lead, and diluted it with an equal quantity of water. The solution was filtrated, and I then added a solution of hepar sulphuris until the brownish-red precipitate which was produced began to fall much paler. After this the liquor was filtrated, and was of a pale beer colour.

I placed it accidentally in an open glass jar, on a shelf near a window, on which the sun shone during a great part of the day, and was surprised to observe that in about two days it began to assume a greenish tinge, which gradually became deeper; on the third day it was of a full green, on the fourth it had a tinge of blue, on the fifth the colour was greenish-

blue, and on the sixth day it was changed to a beautiful deep blue.

The solution continued all the time to be transparent; and although the vessel remained four weeks in the same situation, the blue colour suffered no further change.

This solution much resembles that which SCHEELÉ discovered in the course of his experiments on manganese; but the apparent similar effects, I believe, are produced by opposite causes; for the changes of colour in the alkaline solution of manganese appear to be effected by the absorption of oxygen, but those of the molybdic solution are caused by a diminution of the inherent quantity.

The contrast of the causes which operate on the two solutions becomes the more evident when the effects which acids produce on them are considered; for when a few drops of an acid are added to the solution of manganese, the changes of colour are accelerated, not merely by the neutralization of the alkali and consequent precipitation of the manganese, but (as I conceive) by the accession of oxygen either immediately from the acid, or from the atmosphere, which the manganese is better able to absorb when the disengagement of it from the alkali is thus assisted by the addition of the acid.* On the contrary, if nitric acid is dropped into the molybdic solution, the colour is immediately destroyed, in the same manner as in all the other blue solutions of molybdæna when oxygen is thus presented to them.

The facility with which molybdæna parts with oxygen is evinced not merely in the humid way, for M. PELLETIER found that molybdic acid yielded oxygen to arsenic when

* SCHEELÉ'S *Essays*, p. 108.

distilled with it, and that the latter was converted into a white oxyde.

The same is also proved by my experiments on various oxydes distilled with sulphate of ammoniac ; for the molybdic acid was the only one which could thus be deprived of oxygen, not excepting the tungstic acid, which has been supposed much to resemble that of molybdæna.