

CHEMISTRY

# Molybdenum and Tungsten

## "A Classic of Science"

### Two Elements of Group VI Were Investigated by Scheele, Swedish Apothecary and Pioneer in Chemical Analysis

THE COLLECTED PAPERS OF CARL WILHELM SCHEELLE, Translated from the Swedish and German Originals by Leonard Dobbin. London: G. Bell & Sons, Ltd., 1931. The following are exact reprints of extracts from this publication.

#### Molybdenum

Experiments with Lead-Ore: Molybdaena. Kongl. Vetenskaps Academiens Handlingar. 39 (1778).

DO NOT mean the ordinary lead-ore that is met with in apothecaries' shops, for this is very different from that concerning which I now wish to communicate my experiments to the Royal Academy. I mean here that which in Cronstedt's Mineralogy is called *Molybdaena membranacea nitens*, and with which Quist and others probably made their experiments. The kinds I had occasion to submit to tests were got in different places but they were all found to be of the same nature and composed of the same constituents.

1. (a) I first wished to know how molybdaena behaves in the wet way. For this, it was necessary to get it very finely pulverised. Now since it does not permit of being ground to fine powder by itself, on account of its flexible lamellae, some fragments of vitriolated tartar [potassium sulphate] were also placed in the glass mortar occasionally, when it was at last transformed to a fine powder, which was sifted. Hot water was afterwards poured upon the powder and it was stirred. Molybdaena then sank to the bottom and the solution was poured off. This was repeated several times until no more vitriolated tartar was found in the decanted water, when the powder was dried.

2. I both digested and boiled this mineral with all known acids, but only found two amongst them which have an action upon it, namely, the acids of

arsenic and of nitre. The acid of arsenic does not attack molybdaena before all the water has evaporated. If the heat is then increased a little, arsenic rises into the neck of the retort and, at the end, yellow arsenic is sublimed. Volatile acid of sulphur is obtained in the receiver.

Two parts of fuming acid of nitre were poured upon one part of powder of molybdaena. Scarcely had the mixture in the retort become lukewarm before everything rose together into the receiver with strong heat and dark-red fume. I do not doubt but that the mixture would have taken fire if it had been in somewhat greater quantity. Accordingly, I found it better to use diluted acid of nitre.

3. Six ounces of diluted acid of nitre were poured upon an ounce and a half of pulverised molybdaena. This was placed on a sand-bath, in a glass retort with a luted-on receiver. During digestion the acid would not act, but when the menstruum began to boil, red elastic vapours arose with strong frothing (therefore the retort ought also to be sufficiently large): the acid was abstracted to dryness. The residuum now had a grey colour. The same quantity of diluted acid of nitre was again poured upon it, which frothed with it just as before. This also was distilled off until the remainder was dry, which was now whiter than on the preceding occasion. The same quantity of acid of nitre was again poured upon this and was similarly abstracted. The same operation was repeated for the fourth and fifth times: then at last a chalk-white powder remained. This residuum was edulcorated with hot water until all acidity was gone, and was dried. It weighed six and a half drachms: I shall call it *terra molybdaenae*. The colourless clear edulcorating water was evaporated till half an ounce of it remained behind: it then acquired a fine blue colour, was thick, and contained a little iron. For the rest, it was mostly acid

of vitriol. When the acid was diluted with water, the colour disappeared. Fixed and volatile caustic alkali do not attack molybdaena in the wet way. . . .

7. Earth of molybdaena is of an acid nature. Its solution reddens litmus; soap solution becomes white, and liver of sulphur is precipitated. (b) The solution has also some action on metals. When it is boiled with filings of all base metals, the solution at last becomes bluish. (c) If very little alkali of tartar [potassium carbonate] is added, the earth is dissolved in greater quantity in water, and after cooling crystallises in small confused crystals. This small quantity of alkali brings it about that the earth is not volatilised in the open fire. (d) The solution, while it is still hot, shows its acid property more strongly. It reddens litmus more: it effervesces with chalk, white magnesia, and earth of alum, whence intermediate salts arise which are very difficultly dissolved in water. (e) It precipitates silver, quicksilver, and lead dissolved in acid of nitre; also lead dissolved in acid of salt. These precipitates are reduced upon charcoal, when the melted earth sinks into the charcoal. The other metals are not precipitated, neither is corrosive mercury. (f) The earth of heavy spar, dissolved in acid of salt or of nitre, is likewise precipitated. This precipitate is not regenerated heavy spar [barium sulphate], because it is dissolved by cold water, a property which does not belong to regenerated heavy spar. The solutions of other kinds of earth are not precipitated. (g) The solution also drives out the aerial acid from fixed

**How do we know when a star is coming straight toward us?**

**SIR WILLIAM HUGGINS**

found out by applying the Doppler-Fiveau Principle to stellar spectroscopy. He will tell about it in

THE NEXT CLASSIC OF SCIENCE



KARL WILHELM SCHEELE  
1742-1786

and volatile alkalis; with these it yields neutral salts which precipitate all metallic solutions. Gold, corrosive sublimate, zinc, and manganese are precipitated white; iron and tin in acid of salt, brown; cobalt, rose-red; copper, blue; alum and lime solutions, white. If the sal ammoniac composed of the volatile alkali and the earth of molybdaena is distilled, the earth parts with its volatile alkali at a moderate heat and remains in the retort as a grey powder. . . .

13. After I had now analysed molybdaena and carried out my experiments with its variety of earth, it still remained to be able to recombine this mineral from its proximate constituents. It is known that molybdaena contains sulphur, and my experiments testify the same thing. One part of very finely ground earth of molybdaena was mixed with three parts of sulphur. The mixture was heated on the open fire in a glass retort with luted-on receiver. The retort was so placed at the beginning that the sulphur which rose up into the neck could run back again, but at the

end the sulphur was driven off entirely. The receiver, besides the sulphur, was filled with a suffocating smell of volatile spirit of sulphur. The residuum in the retort resembled a black powder which, rubbed between the fingers, begrimed them with a shining black colour, and for the remainder had the same behaviour in all experiments as natural molybdaena.

Hence we see here a variety of earth which was probably unknown up to the present and which we may call, with reason, acid of molybdaena, since it has all the properties of an acid. But I think I already hear it said: It might be some metallic earth combined with a still unknown acid, or *vice versa*. I leave such and similar views for what they may be worth, so long as there is wanting here convincing proof based upon clear experiments. And although it resembles a metallic earth in certain circumstances, still I believe with confidence that molybdaena consists of an acid mineralised with sulphur.

### Tungsten

*The Constituents of Tungsten.*  
*Kongl. Vetenskaps Academiens*  
*Nya Handlingar.* 2 (1781).

The constituents of this variety of stone seem probably to be still unknown to chemists. Cronstedt enumerates it amongst the ferruginous varieties of stone, under the name of *Ferrum calciforme, terra quadam incognita intime mixtum*. That which I used for my experiments is pearl-coloured and taken from the iron mine of Bitsberg; and as I made many experiments upon it and have ascertained its constituents, I take the liberty of presenting the following to the Royal Academy:

1. (a) In the fire, tungsten does not undergo any perceptible change, neither has glass of borax any special action upon it; (b) but microcosmic salt gives with it, before the blowpipe, a sea-green coloured glass. When such a glass bead is kept in fusion before the outermost tip of a candle flame the colour gradually disappears; a very little nitre also takes away the colour instantly, but it appears again when the blue candle flame is driven upon it. Hence the phlogiston of the flame is the cause of the production of the colour. (c) One part of tungsten finely ground in a glass mortar was mixed with four parts of alkali of tartar [potassium carbonate] and placed in the fire in an iron crucible. When the mixture was

melted, it was poured out upon an iron plate and dissolved in twelve parts of boiling water. Several hours afterwards the ley was poured off from a quantity of white powder which had settled on the bottom. (d) This powder wasedulcorated and acid of nitre was poured upon it until no more effervescence was observed, by which means a great part of it was dissolved. (e) The undissolved powder was dried and again mixed with four parts of alkali of tartar and was melted as on the previous occasion; the mass was dissolved again in water and the powder which remained behind was dissolved in acid of nitre; when only a very little grey powder remained over. (f) The ley (letter c) was saturated with acid of nitre; the mixture then became thick with a white powder, which was washed with cold water and dried. (g) The solution with acid of nitre (letter d) was precipitated with alkali of tartar, when a white precipitate was formed which was dried. . . .

3. (a) The solutions thus prepared with acid of nitre were mixed together and some drops of phlogisticated alkali [potassium ferrocyanide] were added, whereupon about two grains of Prussian blue separated: (b) The mixture was afterwards saturated with caustic volatile alkali [ammonia], but as no precipitate appeared, some solution of alkali of tartar was added; a white powder then separated which weighed, after it was washed and dried, two scruples and five grains. This earth was found to be pure aerated lime; the kind of earth which was obtained according to § 1, letter (g), is also the same. (c) The extracts obtained with volatile alkali were precipitated with acid of nitre; the precipitate was washed with cold water and dried. This precipitate is exactly the same as that mentioned in § 1, letter (f). (d) It is of an acid nature, because it is soluble in water, although about twenty parts of boiling water are required for one part of the precipitate, and it colours litmus tincture red; likewise it has an acid taste. . . .

6. When acid of tungsten is calcined in a crucible, it loses its property of being dissolved afterwards by water. That the acid is inclined to attract phlogiston is seen from the blue colour which it shows in fluxes. . . . Solution of liver of sulphur was precipitated green by our acid, but phlogisticated alkali, white. This latter precipitate is soluble in water. When some drops of acid of salt are mixed with the solution of

this acid in water, and spread upon polished iron, zinc, or even tin, or when these metals are placed in the acid, the acid acquires a fine blue colour.

7. Since the acid of molybdaena also assumes a blue colour from the last-named metals, it is easy to suppose that the acid of tungsten is nothing else than acid of molybdaena. But since in other experiments it behaves quite differently, our acid must also be of a different nature; because (1) the acid of molybdaena is volatile and melts in the fire, which does not occur with acid of tungsten. (2) The first-named acid has a stronger affinity for phlogiston, which is seen from its union with sulphur, and the change it undergoes on calcination with oil. (3) *Calx molybdaenata* does not become yellow with acid of nitre and is dissolved by it quite easily. With tungsten the contrary occurs. (4) *Terra ponderosa molybdaenata* is soluble in water, but not the same variety of earth united with our acid; and (5) acid of molybdaena has a weaker attraction for lime than our acid, because when *calx molybdaenata* is digested with a solution of the previously mentioned sal ammoniac tungsten is again obtained. The iron which is obtained from some sorts of tungsten ought to be regarded as accidentally pertaining to it.

*Science News Letter, April 8, 1933*

## From Page 211

was isolated on special media from the tissue of a microscopically proven carcinoma of the human breast."

Further points to be determined are whether the micro-organism they have described causes the cancer, or whether it is caused by some virus or other germ present in the culture or by some toxin or other substance produced by the bacteria of the culture. It is possible that this culture is not the cause of all types of cancer, but of one group of them. Efforts to develop a serum, either curative or protective, will be a logical outcome of this research.

Investigation of the infectiousness of a type of cancer produced by bacteria as this one was in the guinea pig will also have to be developed.

One of the two physicians making the discovery is from New York while the second is from Philadelphia. They had worked under private research grants for about ten years before bringing their experiments to the National Institute of Health for critical testing.

The story of the development of one kind of cancer in a guinea pig is re-

vealed by daily records in the notebook of Dr. Engle.

These details are given in the Public Health Reports of the U. S. Public Health Service, in which the discovery is being announced to the world.

On Nov. 5, 1932, an adult female guinea pig, a discarded breeder, was inoculated in the mammary region with the germ culture obtained from a proved case of cancer of the human breast.

On Nov. 8, 1932, a condition termed infiltration was observed, by which the investigators could tell that the tissues were being affected.

On Dec. 22, 1932, isolated nodular areas developed in the region.

On Jan. 9, 1933, the nodules were seen to be enlarged and the inguinal glands were affected.

On Feb. 20, 1933, still further increase in size of the tumor and nodules was observed.

On Feb. 24, 1933, the animal was growing weaker.

On Feb. 28, 1933, the animal was very weak and was chloroformed.

Examination post mortem showed tumors in the breast region, inguinal region, kidneys, omentum and within the chest.

The pathologist's diagnosis was: Malignant adenoma with metastasis into the lymph nodes, omentum and kidneys. Commenting on what he found in the animal's body, he said:

"New growth has apparently arisen

ZOOLOGY

# Life of Geologic Past Harvested From Sea Bottom

**H**ARVESTS of "sea lilies," and other strange creatures of the perpetually dark ocean depths have been brought home to the Smithsonian Institution by a recently returned expedition to the waters just north of Puerto Rico, where the deepest part of the North Atlantic Ocean is to be found.

These strange creatures, though called sea lilies, are really animals, relatives of the starfishes. Like them, they have a number of radiating arms, but the arms are branched, and the creatures are attached "bottom side up" to long stalks which anchor them per-

manently to the bottom. Sea lilies, or crinoids as they are also called, were once among the dominators of life on this planet, many millions of years ago. Now, although they are still numerous in the ocean depths, their leadership has been taken away from them by more advanced and active animals.

Upsetting to conventional ideas about cancer is this announcement from the National Institute of Health stating that Drs. Glover and Engle have succeeded in producing cancer in a guinea pig through the use of germ cultures from a human breast cancer case.

This may prove to be the most important news of today or even this year. It is certain that the claims of these two physicians, not government scientists but using Uncle Sam's facilities with the kindly cooperation of the Public Health Service scientists, will meet with opposition from other cancer researchers and practitioners. It is important that such experiments be checked and rechecked by independent experiments. But from such research beginnings have come the conquest of other dread diseases of the human race.

As yet there is no hope for cancer cure or treatment resulting from this work by Drs. Glover and Engle. Cancer patients will only waste time and money by bothering them. Probably there are several different kinds of cancer. The Glover-Engle discovery may mean that one kind of cancer is germ-borne and possibly communicable. But it is much too early to draw conclusions. We can only hope for fruitful results from the beginnings made.

*Science News Letter, April 8, 1933*

There are no plants in the great depths at which the sea lilies grow, for no light ever penetrates to those abysses, and plants cannot grow without light. The whole world of life there consists of animals preying upon other animals, with supplies of carrion plant