XX. On the combinations of antimony with chlorine and sulphur

M. Henri Rose

To cite this article: M. Henri Rose (1826) XX. On the combinations of antimony with chlorine and sulphur, *Philosophical Magazine Series 1*, 67:334, 124-131, DOI: [10.1080/14786442608674027](https://doi.org/10.1080/14786442608674027)

To link to this article: <http://dx.doi.org/10.1080/14786442608674027>

Published online: 10 Aug 2009.

Submit your article to this journal [↗](#)

Article views: 2

View related articles [↗](#)

from Greenwich = $108^{\circ} 6'$. If now we place these three determinations together, we obtain :

	Distance from the Pole.	Long. W. from Greenwich.
1730	$19^{\circ} 15'$	$108^{\circ} 6'$
1769	19 43	100 2
1813	22 50	92 24

Which distinctly shows that this magnetic pole has also a perceptible motion towards the east; and it seems also to follow that it moves away from the terrestrial pole. From the year 1730 to 1796, *i. e.* within 39 years, it has moved $8^{\circ} 4'$, or $12^{\circ} 41'$ in every year more east; from 1769 to 1813, *i. e.* within 44 years, this motion amounted to $7^{\circ} 38'$, or $10^{\circ} 41'$ annually. Whether this difference arises from an inequality in the motion or an error in the observation, we must leave to the decision of future generations.

As the northern pole of the magnetic needle is directed towards this point in the whole of North America, we seem to be justified in concluding, that if we were to travel round it with a compass, the needle would in that time make a complete revolution. If then we are south of this point, the northern pole of the needle will point due north, or in other words, there will be no variation at all on this spot: to the north of it the northern pole would point to the south, or the declination would be 180° ; to the east of it the declination would be 90° W., and to the west it would be 90° E. The justness of this conclusion is proved from the observations of Captains Ross and Parry in the years 1818, 1819 and 1820, some of which are marked on the chart. Most of these arrows, as may be seen, are directed to one point; and the situation of it in the year 1820 might be determined in the manner described above. As these observations are very important for the theory, and we may probably have no speedy opportunity of making observations in these inaccessible parts, I shall proceed to give the most remarkable of them.

[To be continued.]

XX. *On the Combinations of Antimony with Chlorine and Sulphur.* By M. HENRI ROSE*.

I. *Combinations of Antimony and Chlorine.*

WHEN pulverized antimony is distilled with an excess of corrosive sublimate, it is known that there is obtained a solid compound of antimony and chlorine, which melts at a very

* From the *Annales de Chimie*, tom. xxix.

moderate

moderate heat. It attracts the humidity of the air, and is converted into a liquid similar to an emulsion*.

Treated with water it changes, without giving out heat, into hydrochloric acid and a compound of the oxide and chloride of antimony. This white powder, which is precipitated by mixing the chloride with water, is entirely volatilized when heated by a blowpipe in a little matrass; it contains therefore, neither antimonious acid nor antimonic acid: but as this chloride of antimony is converted by water into hydrochloric acid and oxide of antimony, it must correspond to them in composition; and as oxide of antimony contains 3 atoms of oxygen, the antimony must be combined with 3 atoms of chlorine in the solid chloride of antimony, or contain

Antimony	54.85
Chlorine	45.15
	<hr/> 100.00

Yet as Dr. John Davy's analysis of this solid chloride of antimony gives a different result†, I analysed it in the following manner. I poured water on a quantity of the chloride, and added tartaric acid, until the liquid was perfectly clear and ceased to become milky by adding afresh a large quantity of water. I then passed a current of sulphuretted hydrogen through the liquid, till sulphuret of antimony was no longer precipitated. This sulphuret, which was orange-coloured, was washed on the filtre, weighed and dried, then melted in a glass tube; it gave a black sulphuret of antimony, and only traces of sulphur: it was therefore the sulphuret of antimony containing 3 atoms of sulphur, or precisely what ought to be formed under these circumstances. As, however, it contained traces of an excess of sulphur, in consequence of the sulphuretted hydrogen which had been passed for a very long time through the liquid, I heated a part of this sulphuret in a bulb blown in the middle of a glass tube, and passed over it a current of hydrogen dried by chloride of calcium. The sulphuret of antimony was decomposed; and there was obtained antimony, sulphuretted hydrogen, and traces of sulphur.

The liquor, separated from the sulphuret of antimony, was slowly heated, to drive off the sulphuretted hydrogen, but not

* The ordinary butter of antimony in pharmacy, which forms a clear liquid, is not a solution of the solid chloride of antimony in a small quantity of water, but in muriatic acid; for the Pharmacopœias prescribe for its preparation a greater quantity of acid than is necessary for the formation of the solid chloride.

† According to Dr. Davy, the chloride contains:

Antimony	60.42
Chlorine	39.58
	<hr/> 100.00

the hydrochloric acid, which cannot be separated from water by heat when it is mixed with it in small proportion. The hydrochloric acid was then precipitated by nitrate of silver. The chloride of silver obtained had notwithstanding a blackish colour, from a slight mixture of sulphuret of silver. The results of this analysis were: Antimony 1.937 gramme (29.9 grs.), and chloride of silver 6.886 grammes (106.3 grs.), equivalent to 1.699 gramme (24.7 grs.) of chlorine. The chloride of antimony then is composed of

Antimony	53.27
Chlorine	46.73
	<hr/> 100.00

If I had obtained the chloride of silver quite free from sulphuret of silver, this result would agree much more with the calculation.

If a current of dry chlorine is made to pass over heated metallic antimony, another chloride of antimony is obtained. The antimony burns vividly in the gas, emitting sparks, whilst a very volatile liquid is formed. This liquid is white, or of a very light yellowish tint; it also contains chloride of iron, if the antimony employed contained a portion of this metal. The chloride nevertheless remains at the bottom of the vessel, and does not dissolve in the liquid. This resembles, in all its external characters, the fuming spirit of Libavius; it has a strong and disagreeable smell, and fumes in the atmosphere. When exposed to the air, it attracts water and changes into a white mass, in which white crystals form, which afterwards dissolve without rendering the solution milky. This phenomenon is caused by a property of the liquid chloride of antimony, (which it possesses in common with the fuming spirit of Libavius,) of forming a crystalline mass when mixed with a little water.

The liquid chloride of antimony heats strongly when mixed with a greater quantity of water; it becomes milky, and a precipitate is formed having the properties of hydrated antimonic acid. Heated gently, it gives off water and becomes yellowish; but at an elevated temperature it becomes white. The liquid contains hydrochloric acid. As the liquid chloride of antimony is changed by water into the hydrochloric and antimonic acids, which last contains 5 atoms of oxygen to 1 of antimony, it follows that this chloride contains 5 atoms of chlorine to 1 of antimony, or

Antimony	42.15
Chlorine	57.85
	<hr/> 100.00

I analysed

I analysed the liquid chloride of antimony *exactly* in the same manner as the solid chloride. By sulphuretted hydrogen I obtained sulphuret of antimony; also orange-coloured, but a little paler than the sulphuret obtained in analysing the solid chloride. It contained 5 atoms of sulphur to 1 of antimony. Treated with dry hydrogen, it is converted into metallic antimony and sulphur, and sulphuretted hydrogen is disengaged. I obtained 1.980 grammes (30.6 grs.) of metallic antimony; and the liquid, separated from the sulphuret and precipitated by nitrate of silver, gave 11.764 grammes (181.6 grs.) of chloride of silver, equivalent to 2.902 grammes (44.8 grs.) of chlorine. The chloride of silver, however, contained a little more sulphuret of silver than that obtained in the analysis of the solid chloride. The result of this analysis is, then, 40.56 of antimony, and 59.44 of chlorine; which differs from the calculated result: but the difference is produced solely by the sulphuret of silver which is left mixed with the chloride.

It is not the liquid chloride of antimony that is obtained when dry chlorine is passed over sulphuret of antimony containing 3 atoms of sulphur, but it is the solid chloride of antimony and the chloride of sulphur which are formed. The chloride of sulphur may be separated from the chloride of antimony by gently heating them in a very narrow-mouthed matrass: there remains then only chloride of antimony. This is the same product which is formed when gray copper is analysed by chlorine; chloride of antimony containing 3 atoms of chlorine, and chloride of sulphur containing 2 atoms of chlorine only are obtained. There is no double chloride formed, the chloride of sulphur remains on the solid chloride of antimony. Heated gently, so as merely to fuse the chloride of antimony, the latter dissolves completely in the chloride of sulphur, and forms with it a homogeneous liquid; but the chloride of antimony is precipitated in crystals on cooling. This is one way of obtaining large crystals of this chloride; but it must be filtered quickly through blotting-paper, to separate them as much as possible from the adhering chloride of sulphur.

It is remarkable that the liquid chloride of antimony is produced only by the action of chlorine on metallic antimony, but that none is formed if the chlorine is made to act on the sulphuret of antimony.*

II. *Com-*

* I several times passed chlorine over sulphuret of antimony, and always found the same result. I imagined, for reasons which I shall hereafter state, that chloride of antimony with 5 atoms of chlorine was formed. Yet I only obtained chloride with 3 atoms, if I drove off the chloride of sulphur. I was then induced to believe that 2 atoms of chlorine were separated from the chloride of antimony, and had combined with the chloride of sulphur; with

II. *Combinations of Antimony and Sulphur.*

I have made many experiments on the sulphurets of antimony, and only found three which correspond with the oxides of that metal.

The sulphuret of antimony with 3 atoms of sulphur has different colours. That which is found native is of a lead-gray. Its composition has been made known by Berzelius. It is analogous to the oxide of antimony, with 3 atoms of oxygen; for it dissolves without residuum in hydrochloric acid, disengaging only sulphuretted hydrogen.

The same sulphuret of antimony is obtained by passing a current of sulphuretted hydrogen through a solution containing oxide of antimony; but it is of an orange colour, nearly similar to that of the golden sulphuret. It becomes brownish by drying, and then takes an aspect more like kermes. This same sulphuret is obtained by passing sulphuretted hydrogen through a solution of tartar emetic, or through a solution of butter of antimony in water and tartaric acid.

The kermes mineral is, as M. Berzelius first showed, of a composition exactly similar. Its colour, however, is brownish red*.

The derto-sulphuret of antimony with 4 atoms of sulphur is of an orange colour, very like that of the golden sulphuret. It is formed, if sulphuretted hydrogen is passed through a solution of antimonious acid. Nevertheless, tartaric acid must not be added to enable the liquid to be diluted with water, but hydrochloric acid only†. The best way to obtain a solution of antimonious acid, is to dissolve antimony in aqua regia, and to evaporate the solution to dryness. Then the antimonic acid which is formed is changed into antimonious acid by a red heat; this is fused with caustic potash, and the melted mass is treated with hydrochloric acid and water till a clear liquor is obtained. I precipitated this solution by sulphuretted

with which they had perhaps formed a chloride with 4 atoms of chlorine. I therefore passed some chlorine over chloride of sulphur, and carefully purified it by distillation from the sulphur dissolved, in order to detect such a chloride of sulphur. The chloride of sulphur indeed took a little darker colour; but there was no other change, although I made the chlorine pass over it for a long time.

* I analysed a kermes that I had prepared by digesting black sulphuret of antimony with a solution of carbonate of potash. I dried it at a moderate temperature, until it contained no more hygroscopic moisture, and decomposed it by hydrogen. 0.719 gramme (11.1 grs.) of kermes gave me 0.520 gramme (8 grs.) of antimony: its composition then was 72.32 antimony and 27.68 sulphur.

† Very remarkable results are obtained if tartaric acid is added to antimonious acid. — I shall make it the subject of a separate memoir.

hydrogen :

hydrogen: the sulphuret obtained, after being carefully dried, was decomposed by hydrogen. I obtained in one trial 1·305 gramme (20·1 grs.) of antimony from 1·973 gramme (30·5 grs.) of sulphuret, and in another 0·977 gramme (15·1 grs.) of antimony from 1·468 gramme (22·7 grs.) of sulphuret. It is then composed, according to the first trial, of

Antimony	66·14
Sulphur	33·86
	<hr/>
	100·00

and, according to the other, of

Antimony	66·55
Sulphur	33·45
	<hr/>
	100·00

The composition, when calculated, is

Antimony	66·72
Sulphur	33·28
	<hr/>
	100·00

The sulphuret of antimony with 5 atoms of sulphur to 1 of metal, which corresponds to antimonious acid, and which, by calculation, contains 61·59 of antimony and 38·41 of sulphur, is realized in the *golden sulphuret* of the shops. The different methods of its preparation are well known. It is also obtained if a current of sulphuretted hydrogen be passed through solutions which contain antimonious acid: as, for example, that of the liquid chloride of antimony in water, to which tartaric acid has been added. The precipitate obtained is of an orange colour, paler than the precipitate from solutions of oxide of antimony, and does not change colour in drying.

I analysed the golden sulphuret in two ways: I dried it at a heat insufficient to decompose it, till it no longer lost weight. It had then lost all its hygroscopic moisture. I generally made the analysis by passing a current of dry hydrogen over the heated golden sulphuret. Sulphuretted hydrogen was formed, but never water: sulphur was sublimated, and metallic antimony remained. I also analysed it by aqua regia, to which I added tartaric acid. I separated the undissolved sulphur, and precipitated the sulphuric acid by muriate of barytes: this method, however, is slower than that with hydrogen. An exact result is not obtained by fusing the golden sulphuret in a small matrass to convert it into sulphuret of antimony with 3 atoms of sulphur, and calculating the composition of the former from the weight of the latter; not only because the sulphuret of antimony is not absolutely fixed, but also because some oxide of antimony is formed by the air in the matrass,

Vol. 67. No. 334. Feb. 1826.

R

which

which produces a *crocus antimonii* with the sulphur sublimated in its neck.

I do not give the results of the analyses that I made of this sulphuret of antimony at a *maximum*, because they differ very little from the calculated result.

III. Combinations of the Sulphuret of Antimony with Oxide of Antimony.

In the Pharmacopœias, as is generally known, the names of *crocus* and *nitrum antimonii* are given to the compounds in which sulphuret of antimony combined with oxide of antimony in various proportions. Kermes has also been taken for such a compound. M. Berzelius, however, has shown that it does not differ in its composition from the sulphuret of antimony with 3 atoms of sulphur, and the analysis of kermes above given confirms this.

There exists, however, a combination of sulphuret of antimony with the oxide in a definite proportion, and that is the native kermes of mineralogists (*rothspiesglanzerz*). The result of the analysis which I made differs a great deal from Klaproth's, from his having supposed that the whole quantity of the antimony was both oxidated and sulphuretted, and from his having determined the quantity of antimony only*. I analysed the *rothspiesglanzerz* from Braunsdorf, near Freiberg in Saxony, which M. Weiss obligingly gave me for this purpose. The analysis was made by hydrogen, in the same manner as those of the different sulphurets of antimony. I added, however, to the apparatus a weighed tube containing chloride of calcium, to absorb the water formed. I obtained in one experiment 0·676 gramme (10·4 grs.) of antimony, and 0·054 gramme (0·84 grs.) of water, from 0·908 gramme (14 grs.) of the mineral, or 74·45 per cent of antimony and 5·29 of oxygen; and in another, from 0·978 gramme (15·1 grs.) of the mineral, 0·740 gramme (11·4 grs.) of antimony, and 0·047 gramme (0·73 grs.) of water, or 75·66 per cent of antimony and 4·27 of oxygen. I then dissolved 0·340 gramme (5·24 grs.) of the mineral in aqua regia; I added to the solution tartaric acid, and precipitated by muriate of barytes. I obtained 0·517 gramme (8 grs.) of sulphate of barytes, equivalent to 20·47 per cent of sulphur.

If the mean be taken of the oxygen of the first two analyses,

* Beiträge, t. iii. p. 182. The composition of this mineral is, according to him,

Antimony	67·80
Oxygen	10·80
Sulphur	19·70
	<hr/> 98·30

that

that is, 4·78 per cent, and the quantity of antimony required to form the oxide be added to it, the remaining quantity of metal is sufficient (slight errors of observation being neglected) to form with the sulphur the sulphuret of antimony with 3 atoms of sulphur. It will moreover be found, that the quantity of the oxide of antimony is to the quantity of sulphuret as the weight of an atom of the first is to the weight of 2 atoms of the second; so that the native kermes consists of 1 atom of oxide of antimony and 2 atoms of sulphuret of antimony, or of

Sulphuret of antimony . . . 69·86

Oxide of antimony 30·14

The chemical formula is then $\ddot{S}b + 2 Sb s^3$, which M. Berzelius had already assigned for the composition of the native kermes. This composition is remarkable, as it offers the only example of a native crystallized oxy-sulphuret.

XXI. On Mr. BURNS'S *Communications respecting the Double Altitude Problem.*

To the Editor of the Philosophical Magazine and Journal.

Sir,

I CERTAINLY did not intend to notice further the communications of your correspondent Mr. Burns; but I *must* request you to point out a most singular misquotation which he makes from my last letter. I stated that "I noted the mistake in his assumption in italics;" Mr. B. quotes the remark thus, "I noted the assumption in italics."

No person acquainted with what has been done on the double altitude problem, will expect any notice to be taken of Mr. B's third and fourth solutions, as there is nothing new either in the principles of the solution or the formulæ employed.

Your obedient servant,

Greenwich Hospital, Feb. 18, 1826.

E. RIDDLE.

To the Editor of the Philosophical Magazine and Journal.

Sir,

HAVING, with a little surprise, noticed a paper in your very useful work, No. 329, entitled "A short Method of finding the Latitude at Sea by Double Altitudes and the Time between," by James Burns, B.A., I beg leave to say that, though it certainly is a kind of double altitude, which he has investigated, it is not the problem that generally goes under that name, and which is so very puzzling to navigators in general:

R 2

neither