ART. VI.—*On Osmious Acid, and the position of Osmium in the list of Elements*; by J. W. MALLET, Prof. of Chemistry, &c., Univ. of Alabama.

IN most chemical text-books it is stated, on the authority of Berzelius, that there are five oxyds of osmium— OsO , Os_2O_3 , OsO_2 , OsO_3 , and OsO_5 —of which however the second and fourth have not been isolated, although compounds containing them are known. To these may be added a blue substance, first obtained by Vauquelin and supposed by Berzelius to consist of OsO united to either Os_2O_3 or OsO_2 , and the highest oxyd, probably OsO_5 , the existence of which was announced by Frémy in 1854.

While preparing osmium from some black platinum residues I have accidentally obtained, a substance which there is some reason to believe may be osmious acid—the hitherto unisolated teroxyd—mixed indeed with osmic acid, but still permitting certain of its properties to be observed.

Three or four ounces of the platinum residue were treated by a modification of the original process of Wollaston, now seldom adopted. The powder was mixed with three times its weight of nitre, the mixture was fused for some time in an iron crucible, and then poured out upon an iron plate. While still warm the fused cake was broken into fragments and put into a flask fitted with a cork, through which passed a tube two feet long, bent at right angles, and a funnel-tube, the latter drawn out to a very small bore at the lower end, and reaching to the bottom of the flask. The bent tube was well cooled, and *undiluted* oil of vitriol was very cautiously poured, by a few drops at a time, into the funnel.

The acid produced intense heat on coming in contact with the cake of potash salt, and oily drops of a bright *yellow* color began to make their appearance in the cooled tube. These drops very slowly congealed to a solid resembling unbleached bees-wax.

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By the time the sulphuric acid had been added in slight excess a considerable quantity of this yellow substance had collected in the tube and in a receiver attached. By gentle heating the whole was obtained in the receiver, and united under a little water to a single mass. Towards the end of the distillation *colorless* needles and fused drops of the well known osmic acid came over, and doubtless a considerable portion of the yellow mass in the receiver consisted of the same.

At first it seemed probable that the yellow color of the latter was due merely to some impurity, and it was therefore cautiously resublimed, but it again collected of the same tint as before. It appeared to be even more fusible and volatile than osmic acid; it took a long time to congeal under a stream of cold water flowing over the outside of a tube in which it had been melted.

The water in which it was fused acquired a bright yellow color, and gave off fumes, the odor of which seemed to me somewhat different from that of osmic acid, and which irritated the eyes so insufferably that it was scarcely possible to finish work with the acid and put it up for preservation. It was removed as a single cake from the water, and sealed up hermetically in a glass tube which had been previously cleansed with care from all traces of dust or other organic matter. The water in which it had been fused was mixed with caustic potash, and gave a solution of very dark brown-red color, such a tint as would probably result from a mixture of the red* *osmite* of potash discovered by Frémy with the orange-brown *osmiate* of potash.

The sealed tube containing the fused cake or stick of yellow acid was allowed to remain upon a table exposed to the direct rays of the sun. The acid immediately began to sublime upon the sides of the tube, not in long needles and prismatic crystals like osmic acid (which seems to be monoclinic), but in feathery crusts like sal-ammoniac, which under a lens had somewhat the appearance of minute octahedrons grouped together. The color was still bright yellow, but in a short time the sublimed acid began to turn black, and in twenty-four hours the whole inner surface of the tube was perfectly black and opaque. A tube containing pure colorless osmic acid has been exposed in a similar way to the sun for three weeks without any such blackening taking place. A tube closed by a cork, or one from which dust has not been carefully removed will often cause osmic acid to turn dark, but never exhibits anything like the absolute blackness and opacity of the whole tube noticed in the present instance.

* A rose-red color is also characteristic of the salt supposed by Berzelius to be the ammonio-terchlorid of osmium, corresponding in the chlorine series to *osmite* of ammonia.

It is easy however to imagine the cause of this change undergone by the yellow acid if it be in fact the tetroxyd of osmium (mixed with osmic acid). The tetroxyd probably broke up into osmic acid and one of the lower oxyds of osmium or perhaps the metal itself. We might have

In order to ascertain, if possible, which of the above changes had taken place, the tube was opened two or three months after it had been sealed, and the contents were examined. The fused stick of acid was found to be black and partially friable; on heating in another glass vessel most of it sublimed, leaving a little black powder behind, and condensed in needles, still slightly yellowish, but differing little in appearance from common osmic acid. The inner surface of the original tube was found coated with a thin filmy, adherent crust, of a black color and considerable lustre. This was scraped off, and a portion of it gently heated in a stream of dry carbonic acid gas until all traces of adherent osmic acid were driven off. After cooling, the carbonic acid was replaced by dry hydrogen, and heat was again applied. Water condensed on the tube beyond the heated part, thus proving that an oxyd of osmium, not the metal, was under examination. Replacing again the hydrogen by oxygen, osmic acid was produced and carried off with the stream of gas. The black powder scraped off from the original tube was heated with hydrochloric acid, and seemed to be but slowly acted on; the acid however assumed a green color, and hence it is probable that the osmium existed as protoxyd.

It is not easy to see, without further investigation, how osmious acid could have replaced in part osmic acid in the attempt to prepare the latter as above described. Is there a particular stage of the decomposition of nitre by heat at which osmium may replace nitrogen in nitrite of potash (KO, NO_2)? From the relations of the two elements, to be noticed presently, this would seem probable, and in fact Frémy has noticed the crystallization of osmite of potash from a solution in hot water of the fused cake of nitre and iridosmium. A reason for osmic acid (OsO_4) being usually obtained from the latter, instead of osmious (OsO_3), might perhaps be found in the fact that the chemists who of late years have worked upon osmium recommend the use of nitric or nitro-muriatic acid to neutralize the potash—sulphuric acid, to which Wollaston had recourse in his early experiments, is now seldom employed. Thomson, in his "Chemistry of Inorganic Bodies," published many years ago, observes that osmic acid has sometimes a tint of yellow.

It does not seem likely that the cork closing the neck of the flask used for distillation had anything to do with the production of osmious acid, if such took place; the cork itself did not show any appearance of being acted on, and there was no blackening of its surface until some time after the experiment was ended.

The reduction of osmic acid generally results in the formation of the basic oxyds; Berzelius, however, observed that on adding sulphurous acid to a solution of osmic acid the latter passed through various shades of color—*yellow, orange-yellow, brown, green, and at last blue*; he attributed these tints to the successive formation of sulphates of the bin-oxyd, sesqui-oxyd, and blue oxyd; but may not the first step in the reduction have been osmious acid, giving the yellow color?

Another and altogether different view of the nature of the volatile yellow substance above described was suggested as possible by some remarks of Claus in a recent paper on the tendency to reduction of salts of iridium (*Ann. d. Chem. u. Pharm.*, Aug., 1858, S. 129). This author has shown that the platinum metals fall naturally into these groups, in each of which are contained two metals resembling in general habit and relations each other more closely than members of the remaining groups. Platinum and palladium constitute the first of these pairs, iridium and rhodium the second, osmium and ruthenium the third. The atomic weight of the first-mentioned member of each pair is higher than (nearly double) that of the second.

In the paper quoted Claus remarks that the metal of lower atomic weight in each of these groups is much more easily reduced than the other from superior to inferior grades of combination with chlorine; thus the bichlorid of palladium is reduced with much greater ease to proto-chlorid than is the corresponding compound of platinum; and, for the same reason, probably, the bi-chlorid of rhodium is not known, but only the sesquichlorid, while both salts of iridium can be easily obtained. On this same principle Claus explains the fact that no oxyd of ruthenium homologous with osmic acid has been obtained, while he gives the following reasons for suspecting the existence of such an oxyd: "This opinion is based upon the fact, that in my preparation of compounds of ruthenium, which can be obtained only by energetic processes of oxydation, the material worked upon, notwithstanding all my care and economy, gradually diminished, and yet I have never succeeded in collecting a volatile product. Once only, when I had fused ruthenium, perfectly free from osmium, with caustic potash and nitre, dissolved the mass in water, and decomposed it with nitric acid, I observed a peculiar odor, quite distinct from that of osmic or nitrous acid; and afterwards, having covered the beaker, which was smeared on the edge with tallow, with a plate of glass, I

remarked an unmistakable blacking of the tallow, caused by the reduction of a volatile metallic compound."

It seemed possible that the volatile yellow substance to which the present paper refers might have been an acid oxyd of ruthenium*— RuO_3 , RuO_4 , or RuO_5 —and reducible with extreme facility, Claus and others having already noticed the reducing effect of light upon salts of the platinum metals. A portion of the crust from the sides of the tube of yellow acid was carefully examined for ruthenium, the various tests given by Claus as well as that recently proposed by Dr. Gibbs being made use of, but no proof of the presence of this metal could be obtained.

The properties of osmium and its compounds are very remarkable, and render it a matter of no little interest to trace the analogies of this rare substance and fix its place among the other elements. It is described in most chemical works along with platinum and its associated metals, mainly on the ground of community of origin, for in many respects it is unlike the platinum, palladium, rhodium, &c., with which it always occurs in nature. All these metals are commonly thought of as very infusible, of great density, very slightly affected by reagents, and very easily reduced from their compounds to the metallic state; when more closely examined they are found to differ from each other in many of their other properties. The arrangement by Claus of the platinum metals in these groups, each containing one metal of high and one of low atomic weight, viz.

Platinum,	Iridium,	Osmium,
Palladium,	Rhodium,	Ruthenium,

has been alluded to above; the two members of each group are more closely related to each other than to any of the rest. Osmium and ruthenium are clearly the most electro-negative of the series. Graham has inferred the isomorphism of platinum, palladium, iridium and osmium, from the fact that their potassio-chlorids all crystallize in the form of the regular octahedron; the corresponding compound of ruthenium has since been added to the list, while that of rhodium is still unknown. The occurrence of two salts under the same form, *in the regular system*, of

* If such a compound exist, an explanation may be found for the process by which Frémy has obtained a lower oxyd of ruthenium—probably the bin-oxyd—in crystals. He roasts the powder of platinum-residue in a stream of air drawn through a porcelain tube at a bright red heat; osmic acid volatilizes, and is said to carry with it *mechanically* the oxyd of ruthenium, which deposits upon fragments of porcelain placed in the cooler part of the tube. But the oxyd is in distinct crystals, and can therefore scarcely be conceived of as a powder borne along in a merely mechanical way by a stream of vapor; and, moreover, there is no reason for oxyd of ruthenium only being so borne along, while other substances of no greater density remain behind. Is it not more likely that a volatile and very easily reducible homologue of osmic acid is formed, and almost immediately afterwards decomposed, depositing the bin-oxyd of ruthenium?

course does not of itself suffice to establish the relation of isomorphism between them; iridio-chlorid of potassium seems however to be capable of crystallizing in all proportions with the platino- and osmio-chlorids.

The interesting fact has been discovered by Claus that osmio-cyanid and ruthenio-cyanid of potassium are strictly isomorphous with the well-known ferro-cyanid, crystallizing with it in all proportions, and even giving very similar precipitates with various metallic solutions; so that, in these double cyanids, osmium and ruthenium are capable of taking the place of *iron*.

In the greater number of its relations, however, osmium presents itself as a member of the *arsenic group* of elements. This has been noticed by some recent authors, as by Prof. Dana in the arrangement of the elements adopted in his System of Mineralogy, and by Prof. Miller, who says in his lately published Elements of Chemistry that "it presents more analogy with arsenic and antimony than with the noble metals." Frémy too compares osmium in platinum ore to arsenic in the native arseniurets.

Nitrogen, phosphorus, arsenic, antimony, and bismuth are generally recognized as forming a distinct and natural group of elements, and into this group it seems from many considerations that osmium, and probably ruthenium, ought to be introduced. They have some analogies with other natural families, just as arsenic is allied to sulphur in native sulph-arseniurets, and nitrogen and chlorine exhibit some resemblance in the nitrates and chlorates, but here appear to lie their closest relations. It may be interesting to notice some of the principal points of resemblance to or difference from this group.

Iridosmine occurs in crystals closely related in form to those of arsenic, antimony, and bismuth in the metallic state. The analyses of iridosmine are not yet sufficiently numerous or accurate to enable us to decide upon its normal composition, but it seems probable that the two metals occur in variable proportions, and are in this mineral isomorphous, thus establishing, as noticed by Dana, a connection between the arsenic group and that of the distinctly basic metals, as the arsenic and sulphur groups are united through homœomorphous bismuth, tetrady-mite, and tellurium. Dana places iridium in the same section with iron, among the metals whose most stable grades of oxydation are the prot-oxyd and sesqui-oxyd, but the statement of Claus that the *bin-oxyd* of iridium is the most stable and easily prepared compound with oxygen would remove this metal, as also perhaps platinum and palladium, from the iron section to that containing tin and titanium, and the propriety of this transfer may be supported by the relationship of Frémy's crystallized oxyd of ruthenium (doubtless the bin-oxyd) examined

by Sénarmont: This was found to be homœomorphous with stannic and (the rutile form of) titanio acid. The bi-chlorid of tin and potassium too is reported as crystallizing in regular octahedrons, like the corresponding salts of iridium, platinum, and palladium.

The arsenic section, as given by Dana, includes nitrogen, phosphorus, arsenic, antimony, bismuth, osmium, and tellurium. The last-named is marked as doubtful, and should decidedly be placed with sulphur and selenium, to which it is analogous in by far the greater number of its compounds.

In one of the interesting memoirs lately published by Dumas on the numerical relations subsisting among the atomic weights of the elements, the arsenic series is thus given:

				Atomic weights.
Nitrogen,	-	-	-	14
Phosphorus,	-	-	-	14+17=31
Arsenic,	-	-	-	14+17+44=75
Antimony,	-	-	-	14+17+88=119
Bismuth,	-	-	-	14+17+176=207

and the parallelism of this series with that of chlorine, iodine, &c., is supposed to be shown in the following lines:

F (19)	Cl (35·5)	Br (80)	I (127)
N (14)	P (31)	As (75)	Sb (122)

in which a common difference of 5 is assumed between the two members in each of the vertical columns (a difference not strictly brought out in the case of phosphorus and chlorine), and in which antimony is given a higher atomic weight than in the preceding table. Osmium is not included, but in a supplemental note since published we find it placed, with an equivalent somewhat higher than that usually adopted, in the *sulphur* group, serving to complete the following two lines of equivalents:

Mg (12·25)	Ca (20)	Sr (43·75)	Ba (68·5)	Pb (103·5)
O (8)	S (16)	Se (39·75)	Te (64·5)	Os (99·5)

between the paired members of which a common difference of 4 is supposed to exist.

Let osmium and ruthenium be brought into the arsenic group, and the series of atomic weights will then stand thus:

				Atomic weights.
Nitrogen,	-	-	-	14
Phosphorus,	-	-	-	14+17=31
Ruthenium,	-	-	-	14+17+22=53
Arsenic,	-	-	-	14+17+44=75
Osmium,	-	-	-	14+17+66=97
Antimony,	-	-	-	14+17+88=119
Bismuth,	-	-	-	14+17+176=207

The atomic weights of ruthenium and osmium are here assumed as 53 and 97, numbers not differing more widely from those commonly received—52.2 (Claus) and 99.6 (Berzelius)—than do several of those assumed by Dumas. Our knowledge of these two equivalents is based upon very limited data, and can but be looked on as approximative merely. As regards osmium, Frémy says that in several experiments he has obtained an equivalent number lower than that given by Berzelius, and the vapor-density of osmic acid, which we shall notice presently, points to an equivalent close to 97. A re-determination of this equivalent is very much to be desired.

Taking the series as given above, we find ruthenium and osmium to fall in between phosphorus and arsenic—arsenic and antimony; the numbers from phosphorus to antimony increasing by 22—44—66—88, just as in the following group given by Dumas:

			At. wts.
Chromium,	-	-	26
Molybdenum,	-	-	26+22=48
Vanadium,	-	-	26+44=70
Tungsten,	-	-	26+66=92

and we may arrange the two series in parallel lines,

P (31)	Ru (53)	As (75)	Os (97)
Cr (26)	Mo (48)	V (70)	W (92)

These numerical relations are of very little importance in themselves, when we employ the small numbers of the hydrogen scale of equivalents, and especially when we permit ourselves to alter the numbers themselves to any extent, however small, but they acquire more interest when they present us with groupings of elements which we acknowledge on other grounds to be naturally related. In such cases, when the homology is distinctly marked, we may even be justified in taking some liberties for the moment with the numbers standing, often with but slender evidence to support them, for the equivalents of the less-known elements; and we may, perhaps, thus be directed to errors of determination which future experiments will clear away.

The bodies named in each of the two lines just given are homologous in many respects besides that of atomic weight, and a connection between the two series, through vanadium, has lately been shown by Schafarik. There is a clear resemblance running through the formulæ and properties of their oxyds. In the chromium series—a very natural one—the most important oxyds are the metallic acids of the composition MO_3 ; we have also in each case a bin-oxyd, MO_2 ; but the sesqui-oxyd is prominent only in the case of chromium itself, and indicates the relation of this metal with iron.

In the arsenic series the known oxyds are the following:

NO	$\begin{matrix} P_2O \\ PO \end{matrix}$	RuO	AsO(?)	OsO	SbO(?)	BiO(?)
		$Ru_2O_3(?)$		$Os_2O_3(?)$		
NO ₂		RuO ₂		OsO ₂		
NO ₃	PO ₃	RuO ₃	AsO ₃	OsO ₃	SbO ₃	BiO ₃
NO ₄	PO ₄ (?)			OsO ₄	SbO ₄	BiO ₄
NO ₅	PO ₅		AsO ₅	OsO ₅	SbO ₅	BiO ₅ (?)

The prominent compounds in the table are the acids, MO₃ and MO₅; with respect to the separate columns the following facts are noticeable.

The oxyds of nitrogen are well known; the regularity observable in this column causes it to be frequently used as an illustration of the "law of multiples." NO and NO₂ are usually said to be neutral, but the latter plays the part of a base in contact with sulphuric acid, as in the crystals of the oil of vitriol chambers, and possibly the former may do so too in the nitrosulphates (KO, NO, SO₃ and NH₄O, NO, SO₃?) obtained by Davy by bringing nitric oxyd in contact with an alkaline sulphite. NO₃ and NO₅ are well-known acids. It is doubtful whether hypo-nitric acid (NO₄) is capable of combining with bases and forming salts; in contact with the alkalis it yields a mixture of nitrites and nitrates, yet, *when out of contact of bases, it seems to be a body of more stability than either NO₃ or NO₅ (anhydrous).*

In the column of the oxyds of phosphorus, we have first the very anomalous sub-oxyd (P₂O), which is probably the only marked exception to the homology running through the whole table. Before the discovery of red (amorphous) phosphorus by Schrötter this substance was, no doubt, to some extent confounded with phosphoric oxyd, and may even now throw some doubt upon the cases in which the latter seems to have been obtained pure and to have yielded a formula supported by trustworthy analyses. PO, unlike the other protoxyds of the series, is usually considered an acid, but as it has not been obtained in the separate state, and all the hypophosphites contain water, it may be reasonably assumed that the formula of the acid should include hydrogen. PO₄ is doubtful; this may, perhaps, be the composition of Pelletier's phosphorous acid, produced by the slow combustion of phosphorus, a body which undergoes no further oxydation by prolonged exposure to the air, and which, in contact with bases, yields mixed phosphites and phosphates. The last term in the column—phosphoric acid—is well known.

The existence of a distinct protoxyd of arsenic, as of antimony and bismuth, is doubtful. Arsenious acid is *a feeble, volatile, me-*

tallic acid—feeblér in its relations as an acid than arsenic acid, and volatilizing at a lower temperature than the latter. Arsenious acid, moreover, volatilizes at a temperature below that required by metallic arsenic.

In the antimony column, the oxyd SbO_3 is usually viewed as a weak base, but seems also to be capable of uniting as a feeble acid to the alkalies, and even of expelling carbonic acid from their carbonates (Liebig). The iso-dimorphism of SbO_3 and AsO_3 is well established. SbO_3 is volatile at quite a moderate temperature, while metallic antimony requires at least a white heat to vaporize it. SbO_5 is a body of distinctly acid properties. *Both SbO_3 and SbO_5 are converted by heating in the air into SbO_4* ,—the so-called antimonious acid—which seems therefore to be the most stable oxyd when strong bases and acids are not present. It is most probable that, as Frémy maintains, SbO_4 is not itself an acid, but that a so-called alkaline antimonite is in fact a mere mixture of an antimoniate with the compound of antimonious oxyd and alkali ($2\text{SbO}_4 = \text{SbO}_5 + \text{SbO}_3$).

In the bismuth column, the teroxyd is homologous as a base with teroxyd of antimony, but shows little tendency to play the part of an acid with even the strongest bases. This oxyd and the metal itself are volatile at high temperatures. BiO_4 also seems to be devoid of acid properties, but the compound BiO_5 probably exists, and is homologous with SbO_5 , forming alkaline salts of little stability.

Comparing now ruthenium and osmium with the above recognized members of the arsenic group, we find first that both metals form protoxyds, which are feeble bases, as are probably the corresponding compounds of the other members of the group. We next meet with the sesquioxys, whose formula is exceptional in the series, but for neither metal has this grade of oxydation been obtained in the free state and pure, and in the case of osmium its existence may be gravely doubted. Anhydrous Ru_2O_3 is supposed by Claus to be formed during the roasting of metallic ruthenium in the air at a high temperature, but only on the ground that the absorption of oxygen slackens when *about* enough has been taken up to form this compound, and that the proportion necessary for the binoxyd is never fully attained. Claus, however, describes a sesquichlorid with which double salts are formed by the chlorids of potassium and ammonium, and we must therefore assume a sesquioxyd also. Sesquioxyd of osmium is quite unknown in the separate state, and the belief in its existence is founded solely upon the preparation by Berzelius of a dark brown substance, supposed to consist of the sesquioxyd united to ammonia, which, dissolved in hydrochloric acid, yields a brown compound, supposed to be the sesquichlorid of osmium and ammonium. Neither of these, however,

can be crystallized, nor has the constitution assigned to either been supported by an analysis. The so-called ammonio-sesquioxyd detonates when heated, (sometimes with much violence, as I have noticed in removing by heat the deposit of this substance which forms on the end of a retort-neck during the distillation of osmic acid into a receiver containing ammonia,) and hence is probably analogous to fulminating platinum, containing perhaps the binoxyd of osmium. The binoxyd itself is a feeble base, the characteristic color of whose salts in solution is yellow as is the case with the corresponding compounds of iridium. Similar remarks apply to the binoxyd of ruthenium—probably the body obtained, as we have shown, by Frémy in crystals. The teroxyd of osmium is the body supposed to have been isolated in the experiment described at the beginning of this paper. Its position as a feeble acid, capable, however, under some circumstances, of playing the part of a base, its fusibility and volatility (greater, apparently, than those of osmic acid, as nitrous acid is more fusible and volatile than hypo-nitric), its probable crystallization in octahedrons of the regular system, in which arsenious acid and teroxyd of antimony are also found, all tend to indicate homology with the other teroxyds of the arsenic group. The general relations of ruthenic acid, so far as these are known, place it in a similar position. Just as we find hyponitric acid (NO_4) and antimonious acid (SbO_4) to be the most stable of the higher oxyds of nitrogen and antimony, so the well known osmic acid (OsO_4) seems to be the grade of oxydation which osmium most readily assumes and retains when not in contact with bases. OsO_3 and OsO_5 (the latter as described by Frémy) seem scarcely capable of existing in the separate state; when set free from their salts they soon pass into OsO_4 ; while it may as well be doubted that the latter ever exists as a distinct acid in combination with bases as that NO_4 or SbO_4 does so. No so-called osmiate has ever been analyzed; the saturating capacity of the acid, if it be such, is unknown; when free and in solution in water it has no acid reaction, it does not displace carbonic acid from the carbonates, and it is itself expelled by heat from most of its supposed compounds, and is separated in part by water even from potash and soda. No compound of OsO_4 with a base has been obtained in crystals, while Frémy states that he has crystallized the alkaline salts of both OsO_3 and OsO_5 . RuO_4 and RuO_5 are as yet unknown.

The tendency throughout the whole arsenic group is manifestly to the production of the acid compounds MO_3 and MO_5 , the former the more fusible and volatile body, the latter the stronger acid. In addition we have some cases of the protoxyd (MO), a feeble base, and the binoxyd (MO_2), a body of still more feebly basic properties, verging upon the acids. All other grades of

oxydation, so far as they exist at all, may perhaps be correctly viewed as compounds of the preceding *inter se*. The stability of the oxyd (MO_4) in the separate state is remarkable—its formula is one of rare occurrence.

The affinity of all the elements of the group for oxygen is considerable; it is so even in the case of osmium and ruthenium, usually placed among the noble metals. Dumas (*Traité de Chim. app.*) states that osmium does not oxydize at common temperatures, nor even at 100°C ., but I have obtained conclusive evidence that oxydation may go on slowly even at the ordinary atmospheric temperature. The paper label and the cork of a tube containing pure metallic osmium have in the course of several years become blackened, precisely as organic matter is by the fumes of osmic acid, the black tint on the paper decreasing from the mouth of the tube along the outside. A piece of white paper in which some black platinum residue had been wrapped, was strongly stained in the immediate neighborhood of the powder in the course of a few weeks. *The same effect is distinctly observable even upon the paper label placed inside a tube of native iridosmine (Siberian) in the usual coarse grains—a specimen which has lain among other minerals, and has never been placed near any artificial preparations of osmium.* Osmium, like arsenic and antimony, is clearly capable of slowly taking up oxygen at common temperatures. At a red heat, roasting in a current of air affords, as is known, a good method of obtaining osmic acid from the iridosmine of platinum residues—just as by similar roasting arsenious acid is prepared from the native arseniurets.

It would be a matter of much interest to compare osmium with its supposed homologues under circumstances in which we should expect it to play an electro-negative part. Frémy has announced his belief in the existence of an *osmiuretted hydrogen*, but such a body has not yet been isolated and described. Compounds of the metal with ethyl, methyl, &c., would be well worth examination, and it is not unlikely that such might be prepared from a body which in some states of combination exhibits such a high degree of volatility.

The earlier experiments of Deville and Debray upon the platinum metals seemed to have shown that both osmium and ruthenium could be volatilized, at exceedingly high temperatures, without previous fusion; if this were confirmed, a strong point of resemblance with arsenic would be made out, but it appears from a more recent paper that osmium at least may be fused and obtained as a perfectly compact mass, the apparent volatility of the metal being due doubtless to previous oxydation, the crucibles used being permeable to air. We have seen, as regards arsenic and antimony, that their oxyds are more volatile than the metals themselves.

It is lately stated that osmium may be obtained in crystals by the same means as those used for boron and silicon, but I have as yet seen no account of the form which it assumes.

Deville has furnished another interesting fact with respect to osmium, by determining the density of the vapor of osmic acid, which he has found = 8.88. This, if we take the generally received atomic weight for osmium, gives the atomic volume $\frac{131.6}{8.88} = 14.82$, indicating a condensation to 2 vols. If we now calculate back to the theoretical atomic weight we get $(14.57 \times 8.88) - 32 = 97.38$, a number closely approaching 97, which, as we have seen, brings the equivalent of osmium into simple and harmonious relation with those of the other elements of the arsenic group.

The specific gravity of fused metallic osmium having been lately determined by Deville = 21.4, there can be little doubt that all the metals of the platinum family possess the same atomic volume when in the free state, about 4.6 or 4.7; the specific gravity of ruthenium is not yet known with accuracy, but such experiments as have been made render it improbable that it will prove an exception. This number is about one-fourth the mean of the at. vols. of the long recognized members of the arsenic group, but these latter differ so widely among themselves* that the comparison is of little or no value. It would be desirable to get a good determination of the density of osmic acid in the solid state, so that its at. vol. might be calculated and compared with that of antimonious acid.

The specific heat of osmium, so far as its value as a physical character goes, *opposes* the introduction of this element into the arsenic group. It has been determined by Regnault = 0.3063; multiplying now by the equivalent 97, we have the product, 2.9711, thus placing osmium in the list of the elements (including the majority) for which the product of sp. ht. by at. wt. is nearly 3, while for phosphorus, arsenic, antimony and bismuth the product thus obtained is twice as great, or about .6. In this respect, however, osmium probably resembles nitrogen—the latter examined, as it necessarily is, in the gaseous form.

It is to be hoped that the conducting power for heat and electricity of compact osmium will soon be examined; nothing is as yet known of these characters.

* Phosphorus,	$\frac{31}{1.83 \text{ (Schrötter)}}$	= 16.94
Arsenic,	$\frac{75}{5.67 \text{ (Herapath)}}$	= 13.23
Antimony,	$\frac{119}{6.7 \text{ (Karsten)}}$	= 17.76
Bismuth,	$\frac{207}{9.8 \text{ \& Scheerer}}$	= 21.12

Lastly, as regards the magnetic relations of the element—it is placed, with some doubt, by Faraday in the paramagnetic class; the metal and its protoxyd were found to act feebly in this sense, while pure osmic acid is said to have shown itself clearly *diamagnetic*. The strongly diamagnetic character of phosphorus, antimony and bismuth would render a re-examination of this point interesting. Arsenic, however, is said to be very feebly diamagnetic, and is placed by Faraday close to osmium in the list of metals examined, though on the opposite side of the line of magnetic neutrality or indifference.

Reviewing, now, the united physical and chemical characters of osmium, and comparing them with those of the generally recognized members of the “arsenic group,” we are, I think, justified in concluding that here this curious metal should be placed in a natural arrangement of the elements—while important distinctions seem to separate it from some, at least, of the platinum metals, with which it is usually associated and described.

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