ART. X.—*Researches in the Chemistry of Selenic Acid and other Selenium Compounds.* By SIR CHARLES A. CAMERON, M.D., F.R.C.S.I., V.P.I.C.; Professor of Chemistry and Hygiene, R.C.S.I.; and JOHN MACALLAN, F.I.C.; Demonstrator of Chemistry, R.C.S.I.

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THE SPECIFIC GRAVITIES OF THE HIGHER STRENGTHS OF SELENIC ACID.

THE specific gravities of selenic acid for the higher strengths, taken in the liquid state at 15° C., are given in the following table. The most concentrated acid, of 99·73^a per cent. strength, has been referred to when describing the preparation of the anhydrous acid; its specific gravity, 2·6083, was taken while in the super-fused condition. The next acids down to 94·74 per cent. were obtained by diluting that of 99·73 per cent. The acid having a strength of 93·70 per cent. was obtained by heating dilute acid in a vacuum at 100° C., and it supplied the following strengths, down to 82·52 per cent. by progressive dilution. That of 81·73 per cent. was prepared by concentration on the water-bath, and the remaining four by dilution of the latter. Neither the acid heated in a vacuum, nor that which was kept on the water-bath, contained any trace of selenious acid.

TABLE I.

Percentage of Anhydrous Selenic Acid	Specific Gravity
99·73	2·6083
99·08	2·5993
98·68	2·5901
98·16	2·5790
97·37	2·5676
96·97	2·5595
96·16	2·5424
94·74	2·5105
93·70	2·4852
92·83	2·4534
91·59	2·4218

^a 99·73 per cent. of selenic acid, acid sodium selenate, equivalent to 0·07 per cent of neutral sodium selenate, and 0·20 per cent. of water (Se being = 78·87).

Percentage of Anhydrous Selenic Acid	Specific Gravity
90.06	2.3863
89.20	2.3642
88.55	2.3402
87.34	2.3158
86.60	2.2946
85.67	2.2712
84.59	2.2465
83.82	2.2196
82.52	2.1878
81.73	2.1694
80.86	2.1438
79.99	2.1213
79.06	2.0940
73.43	1.9659

Table II. is calculated from Table I., and gives specific gravities interpolated for equal increments of strength. It will perhaps be found most convenient for purposes of calculation, and for showing the relation of the rate of increase of specific gravity to that of the strength.

TABLE II.

Percentage of Anhydrous Selenic Acid	Specific Gravity
99.73	2.6083
99.50	2.6051
99.00	2.5975
98.50	2.5863
98.00	2.5767
97.50	2.5695
97.00	2.5601
96.00	2.5388
95.00	2.5163
94.00	2.4925
93.00	2.4596
92.00	2.4322
91.00	2.4081
90.00	2.3848
89.00	2.3568
88.00	2.3291
87.00	2.3061

Percentage of Anhydrous Selenic Acid	Specific Gravity
86·00	2·2795
85·00	2·2558
84·00	2·2258
83·00	2·1946
82·00	2·1757
81·00	2·1479
80·00	2·1216
79·00	2·0922
73·50	1·9675

The rate of increase of specific gravity is not uniform for equal increments of strength. It diminishes as the strength increases, as in the case of sulphuric acid, but not regularly. The diminution is very marked at the highest strengths. When sulphuric acid has arrived at the greatest strength attainable by ebullition—98·66 per cent., its specific gravity is stated to decrease until the anhydrous acid, H_2SO_4 , is reached. Selenic acid behaves dissimilarly in this respect; the increase of its specific gravity, although not uniform, is maintained throughout.

Berzelius (*Traité de Chimie*, 1830) mentions that selenic acid of 95·9 per cent. strength has a specific gravity of 2·6. Fabian gives 2·609 as the specific gravity of an acid of 94·9 per cent. strength, and 2·627 for an acid of 97·4 per cent. It will be seen that these results do not agree, nor are they consistent with those we have obtained. If values for the strengths mentioned be calculated from the foregoing tables, an acid of 95·9 per cent. will be found to have a specific gravity of 2·5366, while the specific gravities of 94·9 per cent. and 97·4 per cent. acids will be respectively 2·5141 and 2·5680, being less than those assigned above. Furthermore, the difference between the two specific gravities given by Fabian is much less than we find between two acids differing by 2·5 per cent. The most probable explanation of the discrepancy is that the acids which gave the above results contained sufficient selenium dioxide to raise their specific gravities appreciably. It may be shown that the effect of the development of selenium dioxide in selenic acid is to increase the specific gravity relatively to the acidity. In the acids above mentioned, selenium dioxide would exist as such, and not as selenious acid, owing to dissociation of the latter at a temperature below those at which the acids were formed, and the weak affinity for water possessed by the resulting

dioxide. Clausnizer (Liebig's *Annalen der Chemie*, 196, 265) gives the specific gravity of selenium dioxide at 15.3°C . as 3.9538. We have also recently taken its specific gravity, and are in a position to confirm his result. It is thus more than one and a half times as dense as the strongest selenic acid. C. Blarez (*Comptes Rendus*, 103, 804-806) has examined the saturating power of selenious acid. He finds that it is monobasic with cochineal or methyl-orange. With litmus, it is monobasic to ammonia, lime, strontia, and baryta, but with soda or potash the litmus only becomes blue-violet when about 1.5 equivalents of alkali are added. We have obtained a like result with soda or potash and litmus. When one equivalent of the acid is saturated, there is a distinct change in the colour of the litmus, so that in the absence of other acids it might be used as an indicator for selenious acid. Taking 1.5 equivalent of alkali as the limit, the molecule of selenium dioxide in solution will have a less saturating power than that of selenic acid in the ratio of 2 : 1.5. This will be partly counterbalanced by the higher molecular weight of the latter, but the final effect of the substitution of selenium dioxide for selenic acid will be to reduce the acidity. A gravimetric method by which selenium dioxide would be oxidised and estimated as selenic acid, would also show a less acidity compared with the specific gravity than if the pure acid were used, but not to the same extent as when a volumetric process is employed for estimating the strength.

THE ACTION OF HEAT UPON SELENIC ACID.

Action of Heat in a Vacuum.—The effect of heating dilute selenic acid in a vacuum up to 180° has already been described—dilute acid distils until that temperature is reached, when the anhydrous acid remains.

The result of further heating is merely for a time to raise the temperature; the acid does not distil in the anhydrous condition. At about 200° it begins to decompose slowly, and at higher temperatures rapidly, into selenium dioxide, oxygen, and water. The last serves to dilute a portion of the remaining acid, which then at once distils. In order to examine the effect of distilling the anhydrous acid destructively in a vacuum, a portion was heated in a flask connected with a condensing arrangement until rapid decomposition took place. The residue always consisted of a mixture of anhydrous selenic acid with selenium dioxide, the proportion of the latter increasing with the rise of temperature and

length of time of heating. The former was proved to be present by dropping in a crystal of anhydrous acid, when the liquid froze, and it also gave a coloration in the cold with the selenium test for the same acid which will be described hereafter. A portion which had been distilled for some time left a residue of which 0.7107 gram neutralised 18.50 c. c. of seminormal soda solution, using litmus as indicator, equivalent to 94.27 per cent. of acid calculated as selenic—a result which might be expected, owing to the influence of the selenium dioxide in diminishing the acidity, as has been already pointed out. The distillate consisted of selenium dioxide mixed with selenic acid. The latter was in a dilute state, since it would not solidify on addition of a crystal of anhydrous acid, nor would it respond to the selenium test: 0.4703 gram neutralised 11.11 c. c. of seminormal soda solution, equivalent to 85.46 per cent. of acid calculated as selenic. Taking into account the diminution of acidity caused by the selenium dioxide, it is evident that a very concentrated, although not anhydrous, acid distils over.

Action of Heat under ordinary pressures.—When dilute selenic acid is boiled at ordinary pressures nothing but water is evolved until 205° C. is reached, at which temperature it has the composition of the monohydrated acid. In these respects it behaves like dilute sulphuric acid. After passing 205° C. the distillate contains at first mere traces of selenic acid, but its strength gradually increases. A portion of acid distilled between 205° C. and 227° C. yielded a distillate of which 0.6826 gram neutralised 0.10 c. c. of seminormal soda solution, equivalent to 0.53 per cent. of selenic acid. On further heating from 227° C. to 260° C. a distillate was obtained, of which 0.3818 gram neutralised 0.32 c. c. of seminormal soda solution, equivalent to 3.03 per cent. of selenic acid. At the latter temperature the acid commenced to distil over in white fumes. 0.6878 gram of the residue left at 260° C. neutralised 17.76 c. c. of seminormal soda solution, equivalent to 93.41 per cent. of selenic acid. At higher temperatures a portion of the acid is decomposed, the distillate being kept weak by the water continuously set free in the decomposition; and at still higher temperatures much selenium dioxide also distils over. A portion of acid which commenced to boil at 235° C. was heated until the temperature rose to 325° C.: 2.1542 grams of the distillate neutralised 3 c. c. of seminormal soda solution, equivalent to 5.04 per cent. of selenic acid. The residue was then further heated until the greater

part of the acid was decomposed, and the strength of the distillate taken: 1.6176 gram neutralised 16.5 c. c. of semi-normal soda solution, equivalent to 36.90 per cent. of acid calculated as selenic, but much of the acidity was due to selenious acid, a large amount of which was present in the distillate. It is thus seen that the acid which distils under ordinary pressures is always highly dilute.

When anhydrous selenic acid is strongly heated under ordinary pressures a portion of it is decomposed into selenium dioxide, oxygen, and water, the latter serving to dilute the remaining acid. It will then no longer solidify on addition of a crystal of the anhydrous acid. After further heating it becomes sufficiently dilute to distil over in the manner already described. It is instructive to compare with this the action which takes place in the case of anhydrous sulphuric acid. Marignac found (*Annales de Chimie et Physique*, (3), 39, 184), that the latter when heated gives off sulphuric anhydride until the remaining acid is reduced to the same strength as that yielded by a more dilute acid on prolonged ebullition—about 98.66 per cent. In the case of selenic acid the anhydride is evidently unable to exist free at elevated temperatures, but breaks up into selenium dioxide and oxygen.

It is worthy of note that a remarkable coincidence exists between the temperature at which selenic acid is decomposed and that at which selenium dioxide sublimes. The latter is not stated very definitely in any of the chemical text-books; we have found, however, that at 280° C. rapid sublimation takes place, while at 250° C. volatilisation proceeds slowly. When selenic acid is kept for some time at the latter temperature it is always found to contain traces of selenium dioxide, while at 280° C. decomposition proceeds with rapidity. It is probable that a connection exists to a considerable extent between the phenomena, and that the explanation of the coincidence may be that the comparatively weak affinities which bind the molecule of selenic acid are unable to prevent its disruption when once a temperature is reached at which the tendency of its constituents to separate is aided by the expansion attending a change to the gaseous condition. We have seen that both phenomena are affected by the temperature; they are also dependent to some extent upon the pressure. Anhydrous selenic acid commences to dissociate in a vacuum at about 200° C. We found that when selenious acid was heated under similar circumstances water was quickly evolved, and after prolonged

heating of the residue a distinct white ring of selenium dioxide was deposited on the cold portion of the neck of the flask.

THE ACTION OF SULPHUR UPON SELENIC ACID.

When powdered sulphur is mixed with liquid anhydrous selenic acid, there is no action in the cold; but if the mixture is heated to 63°C ., the sulphur dissolves in the acid with production of an exceedingly deep indigo-blue colour. There is some action, but slight, at 58°C . The body which is produced is very unstable, since it begins to decompose at the temperature at which it is formed, with evolution of sulphur dioxide, and reduction of the selenic acid to selenious acid. If water is added when the colour has first developed, sulphur is deposited in soft yellow flakes; but after decomposition has commenced, the addition of water throws down red selenium chiefly, owing to the reaction between the sulphurous and selenious acids which are formed.

A similar action has long been known to occur between sulphur and sulphuric acid. In 1804 Buchholz (Gehlen's *Neues Journal der Chemie*, 3, 7), discovered that sulphur dissolved in the latter acid with the formation of a blue colour, the sulphur being reprecipitated on addition of water. This reaction was subsequently investigated by Vogel, Schweigger, Berzelius, Wach, and Stein, and in 1875 Weber succeeded in isolating the blue compound (Poggendorff's *Annalen der Physik und Chemie*, 156, 531), and discovered it to be a sesquioxide of sulphur, S_2O_3 , but very unstable, decomposing at ordinary temperatures with evolution of sulphur dioxide.

THE ACTION OF SELENIUM UPON SELENIC ACID.

A reaction takes place between selenium and anhydrous selenic acid in the cold. The selenium dissolves in the acid with production of an intense and beautiful green colour. The presence of a minute quantity of water prevents the colour from developing fully until the acid is warmed. The acid is capable of dissolving a considerable quantity of selenium. If kept in a closed vessel the colour thus produced is very permanent, being unaffected for months during summer weather, but if the acid be heated to 75°C . the colour disappears, and the selenic acid is found to be partly reduced to selenious acid. Addition of water, when the colour has developed, throws down a voluminous red precipitate of selenium; and exposure to the air in an open vessel for a few

minutes is sufficient, from the same cause, to change the green colour to red. It will be shown hereafter that this green colour is probably caused by the formation of a new oxide of selenium. Its production with the anhydrous acid affords a test for the latter, which we have already made use of in examining the effect of heat upon selenic acid.

In 1827 Magnus found that selenium was dissolved by strong sulphuric acid, with development of a green colour, and was reprecipitated on addition of water. Berzelius and Fischer subsequently investigated the reaction, and in 1875 Weber (Poggendorff's *Annalen der Physik und Chemie*, 156, 545), isolated the green compound, and found it to be a sulphoxide of selenium, SeSO_3 . The colour given by selenium with sulphuric acid is a dark green, not so bright as that which it produces with selenic acid.

THE ACTION OF TELLURIUM UPON SELENIC ACID.

Like selenium, tellurium reacts upon anhydrous selenic acid in the cold, but with production of a purple red colour. Even when the acid is not perfectly anhydrous, it will still give a coloration in the cold. The compound thus formed is probably very unstable, since the colour disappears at so low a temperature as 19°C ., the selenic acid being partly reduced to selenious acid. If water is added when the colour has developed, tellurium is thrown down in sooty flakes, and exposure to moist air produces the same effect.

Tellurium reacts in a similar manner with strong sulphuric acid, with development of a red colour, and reprecipitation on addition of water. This was first observed by Müller von Reichenstein. In 1798 the same reaction was investigated by Klaproth, and afterwards by Magnus and Fischer. The red compound was isolated by Weber in 1882 (*Journal für praktische Chemie*, 25, 218), and soon afterwards independently by Divers and Shimosé (*Journal of the Chemical Society, Transactions*, 43, 319), and was ascertained to be tellurium sulphoxide, TeSO_3 .

COMPARISON OF SULPHOXIDES WITH SELENOXIDES.

The coloured compounds first formed by the action of sulphur, selenium, and tellurium upon sulphuric acid were subsequently produced by the action of the same bodies upon sulphuric anhydride, and were isolated by forming them in the latter manner, and then removing the excess of anhydride. As has been already mentioned, they were found to be sulphoxides having the composition respec-

tively, SSO_3 , SeSO_3 , and TeSO_3 . Considering the similarity of the reactions which produce them, and of the decompositions to which they are liable, it is very probable that the coloured bodies formed with selenic acid are selenoxides, analogous to the sulphoxides already known, the sulphur in the latter being replaced by selenium. A comparison of the formulæ of the two series of bodies as represented in the following table, leads to some interesting considerations:—

Colour of Compound	Sulphoxides	Selenoxides
Blue	SSO_3	SSeO_3
Green	SeSO_3	SeSeO_3
Red	TeSO_3	TeSeO_3

The green body formed by the action of selenium upon selenic acid is, in all probability, a new oxide of selenium, having the composition Se_2O_3 , analogous to the sesquioxide of sulphur formed by the action of sulphur upon sulphuric acid.

The colour of the above compounds appears to be almost entirely due to the element which is added on to the anhydride; the sulphur or selenium in the residual portion of the molecule has scarcely any effect upon the colour.

The green body SeSO_3 must be isomeric with the blue compound SSeO_3 , and consequently the atoms of sulphur and selenium in each of these bodies must occupy dissimilar positions in the molecule.

THE POSSIBLE EXISTENCE OF SELENIC ANHYDRIDE.

A consideration of the forgoing facts leads to the conclusion that selenic anhydride, which has not up to the present time been obtained, is yet capable of existing in a free condition. Just as the sulphoxides are direct addition compounds of sulphur, selenium, and tellurium respectively, with sulphuric anhydride, so the selenoxides must be regarded as addition compounds of the elements mentioned, with selenic anhydride. It is difficult to conceive that bodies so constituted are capable of existing free, and that the anhydride is unable to do so. On the other hand, it is probable that it dissociates at a comparatively low temperature, but one that is higher than 75°C .—the highest temperature at which the most stable of the selenoxides has been as yet found to exist. Selenious anhydride is always obtained, and not selenic, under similar conditions to those which produce sulphuric anhydride, and involving a high temperature.

We have examined the action of heat upon various selenates. Those selected for the purpose were the selenates of antimony, bismuth, platinum, lead, and silver, and also ferric and mercuric selenates. In no instance was selenic anhydride obtained, but selenious anhydride was evolved in all cases when the above selenates were strongly heated.

V. Gerichten (*Liebig's Annalen der Chemie* for 1873, p. 214) endeavoured to form selenic anhydride in a similar manner to that by which sulphuric anhydride is usually obtained—by leading a mixture of oxygen and the vapour of selenious anhydride through red-hot platinum sponge. He states that in one experiment a white deposit was obtained which consisted partly of selenious anhydride, but probably also contained selenic anhydride, since it dissolved in water with a hissing sound, and the solution was found to contain selenic acid. In subsequent experiments a decidedly negative result was obtained, since only selenious anhydride was found in the product.

In order to examine if selenic anhydride is produced in the manner just described, the following experiments were made:—

Some platinum sponge was introduced into a combustion tube, and a quantity of selenious anhydride placed behind it. The platinum sponge was kept at a red heat, and the selenious anhydride was also heated until it sublimed. Oxygen, which was first dried by passing through a series of tubes containing calcium chloride and sulphuric acid, was led through the platinum sponge, carrying the vapour of the selenious anhydride with it. A white deposit formed in front of the platinum sponge, which, on examination, was found to consist solely of selenious anhydride. The experiment was repeated, substituting selenium for selenious anhydride. The vapour of the selenium, on passing through the platinum sponge, was oxidised to selenious anhydride, but no selenic anhydride was formed.

The next experiment was similar to the first, but platinum black was substituted for platinum sponge. As before only selenious anhydride was deposited.

In the next experiment selenious anhydride was mixed with platinum sponge, and placed within a tube arranged in such a way that it could be placed in an oil-bath. The temperature was then raised gradually to 250° C., oxygen being led through continuously. At the temperature mentioned a sublimate formed, and this, as well as the platinum sponge, was treated with water and tested, but no selenic acid was found.

The next experiment was similar to the last, except that the selenious anhydride was mixed with platinum black instead of platinum sponge, but, as before, nothing but selenious anhydride was obtained.

As may be seen from the above experiments, we have been unable to confirm the observation made by V. Gerichten.

We have found that oxygen in the active condition is unable to oxidise selenious anhydride. Oxygen, which was first passed through a series of drying tubes, was ozonised by means of a Houzeau's ozoniser, and then led slowly through a tube containing selenious anhydride for three hours and a half. At the end of that time the tube was disconnected, the ozone displaced by a current of dried air, and the contents of the tube dissolved in water and tested for selenic acid, but no trace of it was detected.

THE SELENATES OF ANTIMONY, BISMUTH, AND PLATINUM.

In the examination of the action of heat upon selenates, the three above mentioned were included. We have been unable to find any published account of these, and accordingly give here a short description of them.

Antimonious selenate.—This body was formed by heating metallic antimony with selenic acid until it dissolved, and then continuing the heating until the excess of acid was driven off. It forms a white crystalline mass, which under the microscope is seen to consist of minute prisms. It is not very soluble in acids, but on boiling with selenic acid for some time it dissolves slightly, but apparently without formation of an acid salt, as the crystals deposited on evaporating the solution have the same shape and size as the original salt. It is not decomposed on boiling with water, nor is it soluble; if, however, the excess of selenic acid has not been expelled in its preparation, a little of it dissolves in the weak acid formed, and crystallises out again on cooling.

Bismuthous selenate.—This was prepared by boiling bismuthous carbonate with selenic acid, and continuing the heating until the excess of acid was expelled. It crystallises in minute white prisms. It is insoluble in water, and is not decomposed by it on boiling, but if selenic acid is present it dissolves. It is also soluble in sulphuric acid on boiling, and readily in hydrochloric and nitric acid. Potash and soda decompose it, uniting with the selenic acid.

Platinic selenate.—This was prepared by heating platinic chloride with selenic acid until the hydrochloric and excess of selenic acid

were expelled. It is a dark-brown body, which dissolves slightly in water on boiling, forming a yellowish-brown solution. It is insoluble in alcohol. It dissolves readily in hydrochloric acid, and leaves metallic platinum on ignition.

THE ACTION OF PHOSPHORIC ANHYDRIDE UPON SELENIC ACID.

When sulphuric acid is heated strongly with phosphoric anhydride, sulphuric anhydride is evolved; on the other hand, the effect of heating a mixture of anhydrous selenic acid and phosphoric anhydride to a high temperature is, that selenious anhydride is given off, and not selenic. In order to see if a different reaction occurs between the latter two bodies at a lower temperature, some anhydrous acid was mixed with phosphoric anhydride in a flask, which was then tightly closed and placed in the water-oven. After heating for some time a clear solution was obtained, and the flask was then removed and allowed to stand in the cold. Crystals were slowly deposited, which under the microscope were seen to be transparent cubes. The acid liquid was drained off, and the crystals examined. So far as an analysis could be carried out the result agrees with the view that the body thus obtained is selenic anhydride, SeO_3 , but the quantity of material at our disposal at the time was too small to admit of its satisfactory separation and examination. We are, however, at present engaged in operating upon larger quantities, and hope, at no distant date, to submit our results to the Royal Society.

SELENIUM OXYCHLORIDE.

It may be useful here to mention a reaction, hitherto undescribed, by which selenium oxychloride can be obtained. It consists in distilling a mixture of sodium chloride and selenium dioxide. The reaction is a simple one—

Half the selenium remains as sodium selenite.