# **245.** *The Determination of Selenate, and the Preparation of Some Aluminium Selenates.*

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The determination of selenate by reduction to selenium with concentrated hydrochloric acid and sulphur dioxide in one operation is found to be much simpler and more satisfactory than the other methods which have been recommended. Normal aluminium selenate has been prepared and found to have, in its usual hydrated form, the formula $Al_2(SeO_4)_3,16H_2O$. It is thus analogous to the sulphate with which it is isomorphous. The well-crystallised double salt $NaAlSeO_4,11H_2O$ has also been examined. The compound $Al_2O_3,2SeO_3,11H_2O$ has been prepared and shown to be similar in every way to the corresponding basic sulphate; and $5Al_2O_3,6SeO_3,40H_2O$ has also been obtained.

Selenate alunites are formed under similar conditions to the ordinary alunites and, like them, show a variable composition owing to the various types of replacement which can occur in the alunite lattice.

*Analysis of Selenates.*—Many methods have been recommended for the determination of selenates, most of which we have examined.

Barium selenate is considerably more soluble, and silver selenate is much less soluble, than the corresponding sulphate. Neither compound is sufficiently insoluble to be really suitable for the direct determination of selenate although it is possible, by precipitation and weighing as either of these compounds, to obtain results for selenate correct to about 1%. Solutions must not be too dilute, considerable excess of precipitant must be used, and the precipitates must be washed with the minimum amount of water (or acetone plus water) previously saturated with barium or silver selenate.

The other methods for determining selenate involve reduction to selenium which is then weighed. Hydrazine sulphate has been used for this purpose (Schoeller and Powell, "The Analysis of Minerals and Ores of the Rarer Elements," 1940, p. 178) but we found reduction extremely slow and the method very unsatisfactory. The more usual methods involve reduction to selenium in two stages, by hydrochloric acid followed by sulphur dioxide. Reduction to selenious acid by concentrated hydrochloric acid is rapid on heating but involves danger of loss of volatile chlorides or oxychloride of selenium. To avoid this, Hillebrand and Lundell ("Applied Inorganic Analysis," 1929, p. 259; see also Mellor and Thompson, "Quantitative Inorganic Analysis," 2nd edn., 1938, p. 483) digest, at below 100°, a solution which is less than 6N. with respect to hydrogen chloride. Digestion is continued until liberation of chlorine can no longer be detected with starch–iodide paper. This takes six or more hours but results appear to be reliable. The obvious way to avoid both slowness of reduction and loss of volatile selenious compounds was to combine the two reduction stages by the use of concentrated hydrochloric acid previously saturated in the cold with sulphur dioxide, and we find this to be by far the simplest method for determining selenate.

Our usual procedure was to use 25 c.c. of the concentrated $HCl-SO_2$ mixture for 1 g. of solid selenate or 50 c.c. for 25 c.c. of an aqueous solution. Separation of red selenium began almost at once. Since the sulphur dioxide reacts at once with both products—chlorine and selenious acid—of the primary reaction, precipitation of selenium is very rapid. The mixture was usually left overnight at room temperature but two hours' storage was found to be ample. It was then heated on the hot plate to drive off sulphur dioxide and much of the hydrochloric acid, and to convert the selenium into the grey form. Water was then added to make a volume of about 50 c.c., which was gently boiled for some time to facilitate removal of soluble matter from the selenium. The latter was collected in a Gooch crucible, washed with water till free from chloride and then with alcohol, and dried at 100—110° to constant weight. After the above method had been developed it was found that Vogel ("Textbook of Quantitative Analysis," 1939, p. 527) gives essentially the same method for the separation and determination of selenate in presence of tellurate, but, curiously enough, for the determination of selenate in other, more ordinary, circumstances only the unsatisfactory two-stage reduction processes are given. It should be strongly emphasized that the new process is greatly superior to these and is a very simple operation.

*Aluminium Selenates.*—An *X*-ray crystallographic study of the compound $Al_2O_3,2SO_3,11H_2O$ had shown that distinction between the aluminium and sulphur atoms in the crystal lattice was difficult. This was the origin of the work now described on some of the aluminium selenates. The heavy selenium atoms in the selenates are much easier to locate than the sulphur atoms in the isomorphous sulphates. Sufficient work has been carried out to show that the basic salts existing in the system $Al_2O_3-SeO_3-H_2O$ are probably of the same types as the corresponding sulphates, with very similar molar solubility and general relationships.

By working on similar lines and with similar concentrations to those found to give good results with the sulphates there should be little difficulty in preparing most of the analogous selenates.

It is, however, unfortunate that basic selenate solutions cannot be prepared by the action of amalgamated aluminium on selenic acid because of the ease with which the latter is reduced.

$Al_2(SeO_4)_3,16H_2O$. Many selenates are well known. Berzelius (*Pogg. Ann.*, 1834, **32**, 11) seems to have been the first to prepare the aluminium compound and show that it was similar to the corresponding sulphate in its properties and reactions. The degree of hydration of both salts has been uncertain. Since the sulphate has only 16 molecules of water of crystallisation and not the 18 often ascribed to it (Bassett and Goodwin, *J.*, 1949, 2245), it was probable that this would apply also to the *selenate*, which has therefore been prepared and examined.

A solution of aluminium nitrate was precipitated at room temperature with a moderate excess of ammonia, and the hydroxide well washed with cold water. Selenic acid ($H_2SeO_4$, 41·2%) in small excess was added to the moist hydroxide, and the mixture digested till most of the solid had dissolved. It was then filtered. The solubility and general properties of the aluminium selenate are very similar to those of the corresponding sulphate and, although it can be readily separated in a pure condition, well-formed, large crystals are not obtainable. The general procedure for obtaining the crystalline compound from its solution is essentially the same as that used for the sulphate. The solution is evaporated to a small bulk and allowed to crystallise. The crystals are well drained on the pump, washed with alcohol of increasing concentration, and air-dried. Additional amounts of the selenate can be recovered from the mother-liquor by slow addition of several volumes of alcohol. The crystals so obtained are similar in every way to those of the sulphate $Al_2(SO_4)_3,16H_2O$ and give an *X*-ray diagram which shows that the two compounds are truly isomorphous [Found : $Al_2O_3$, 13·23; $SeO_3$, 49·05 (Se, 30·51). $Al_2(SeO_4)_3,16H_2O$ requires $Al_2O_3$, 13·22; $SeO_3$, 49·41 (Se, 30·74)%. Calc. for $Al_2(SO_4)_3,18H_2O$ : $Al_2O_3$, 12·64; $SeO_3$, 47·21 (Se, 29·36)%]. It is evident that the selenate contains only $16H_2O$ and not 18.

Collet (*Compt. rend.*, 1949, **228**, 1122) found, in the system $Na_2SeO_4$–$Al_2(SeO_4)_3$–$H_2O$ at 20°, three solid phases, *viz.*, $Al_2(SeO_4)_3,22H_2O$; $Na_2SeO_4,Al_2(SeO_4)_3,22H_2O$, and $Na_2SeO_4,10H_2O$. As no analytical data were given it is not possible to say whether the 22 in the $Al_2(SeO_4)_3,22H_2O$ is a misprint. This may be doubted since the same formula is given in connection with the system $Na_2SO_4$–$Al_2(SeO_4)_3$–$H_2O$; $Al_2(SO_4)_3,18H_2O$ is said to occur in the system $Na_2SeO_4$–$Al_2(SO_4)_3$–$H_2O$. Only in the case of $Na_2SO_4,10H_2O$ and $Na_2SeO_4,10H_2O$ is any formation of mixed crystals noted in the mixed sulphate–selenate solutions, and the isothermal of the system $Al_2(SO_4)_3$–$Al_2(SeO_4)_3$–$H_2O$ is said to consist of two curves corresponding to the two hydrated aluminium salts [presumably $Al_2(SO_4)_3,18H_2O$ and $Al_2(SeO_4)_3,22H_2O$]. This seems remarkable in view of the undoubted isomorphism of $Al_2(SO_4)_3,16H_2O$ and $Al_2(SeO_4),16H_2O$ which are the compounds we have obtained at room temperature from pure sulphate or selenate solutions.

Aluminium *iso*propoxide is now obtainable commercially as a very pure product and is convenient for preparing aluminium selenate. The selenic acid available contained $SeO_3$, 35·93%, and the aluminium *iso*propoxide contained $Al_2O_3$, 25%. Quantities of the two reagents were taken calculated to give a small excess of selenic acid. On mixing, all at once, there was a moderate evolution of heat. An equal volume of water was then added, and the mixture boiled gently until all but a small amount of white flocculent solid had dissolved. This was removed by filtration. An almost theoretical yield of the aluminium selenate was obtained by evaporation and crystallisation of the solution, followed by treatment of the mother-liquor with several volumes of alcohol. A preparation obtained by this method contained $Al_2O_3$,13·25; $SeO_3$, 49·49 (Se, 30·79)%. It is very important when preparing $Al_2(SeO_4)_3,16H_2O$ to make sure that there is a small excess of selenic acid, for otherwise the first crystals to separate consist of the basic salt $Al_2O_3,2SeO_3,11H_2O$. The prisms of this salt are easily distinguished from the small, usually six-sided, plates of $Al_2(SeO_4)_3,16H_2O$, but unless the early stages of the crystallisation are seen they can be easily missed.

$Al_2O_3,2SeO_3,11H_2O$ [$AlOH(H_2O)_5SeO_4$]. The conditions under which $Al_2O_3,2SeO_3,11H_2O$ could separate as a stable solid phase were unknown but would be very restricted to judge from the 25° isothermal of the system $Al_2O_3$–$SO_3$–$H_2O$. A solution containing $Al_2O_3$, 7·6; $SO_3$, 17% would be in equilibrium with $Al_2O_3,2SO_3,11H_2O$, and the equivalent selenate solution might be expected to be in equilibrium with $Al_2O_3,2SeO_3,11H_2O$.

The proportions of reagents used in the following preparation were calculated to give, after concentration, 50 g. of the above-mentioned selenate solution and 2 g. of $Al_2O_3,2SeO_3,11H_2O$.

2·25 G. of aluminium were dissolved by heating in 112 c.c. of 2·05N-hydrochloric acid. This solution was then made to react with 41·27 g. of silver selenate (the theoretical amount). Interaction is slow and difficult owing to the very small solubility of the silver salt (1·182 g./l. of water at 20°; Lenher and Kao, *J. Amer. Chem. Soc.*, 1925, **47**, 1521). 10 G. at a time of the silver selenate, contained in a Gooch crucible, were suspended just beneath the reflux tube attached to the flask in which the aluminium chloride solution was gently boiled. In this way the silver selenate was slowly dissolved and made to react with the chloride solution. It took 50—60 hours for each 10 g. of silver selenate to react. Boiling was stopped every evening, and the silver chloride which had separated from the mixture in the flask was filtered off every morning before boiling was restarted. Even then much bumping occurred at times, so that a considerable amount of silver chloride formed inside the Gooch crucible. When all the silver selenate seemed to have dissolved, the residual material in the crucible was tipped into the solution and digested with it for 8 hours in order to dissolve any silver selenate which might still be present. After the whole 41·27 g. of silver selenate had been made to react, the filtered solution was evaporated down till it weighed 45 g., and then shaken at 25° in a thermostat.

The crystals which separated were washed with alcohol of increasing concentration and air dried (yield 1·2 g.) [Found : $Al_2O_3$, 18·45; $SeO_3$, 46·23 (Se, 28·75). $Al_2O_3,2SeO_3,11H_2O$ requires $Al_2O_3$, 18·41; $SeO_3$, 45·84 (Se, 28·57)%]. The ***basic selenate*** forms monoclinic prisms looking just like those of the corresponding sulphate. *X*-Ray examination showed that the two compounds are strictly isomorphous with unit cells of almost the same dimensions.

The equilibrium solution from which the selenate had separated contained $Al_2O_3$, 5·59; $SeO_3$, 20·66%. This gives $SeO_3/Al_2O_3 = 2{\cdot}97$, whereas the $SO_3/Al_2O_3$ ratio for solutions in equilibrium with $Al_2O_3,2SO_3,11H_2O$ at 25° ranges from 2·69 to 2·95 (Bassett and Goodwin, *loc. cit.*, p. 2245).

$Al_2O_3,2SeO_3,11H_2O$ is prepared in larger amounts more readily from selenic acid and aluminium hydroxide or aluminium *iso*propoxide. Owing to the short range of solutions with which this compound can be in equilibrium, it is always advisable to collect the crystals which separate in two or three fractions. Even when the greatest care is taken in making up the mixtures there is always the certainty that $Al_2(SeO_4)_3,16H_2O$ will begin to separate out if evaporation and crystallisation is allowed to proceed too far, and if the initial mixture was rather too basic the first crystals to separate may consist of some more basic salt—which our observations suggest is almost certainly $5Al_2O_3,6SeO_3,xH_2O$, analogous to the corresponding basic sulphate. It is essential in order to guard against this possibility that the $SeO_3/Al_2O_3$ ratio of the initial mixture should be not less than that of the solution in equilibrium with both $Al_2O_3,2SeO_3,11H_2O$ and $5Al_2O_3,6SeO_3,xH_2O$ at the temperature of crystallisation. This value is unknown for the selenates but may be taken to be about 2·7 at 25° from analogy with the corresponding sulphates, while the $SeO_3/Al_2O_3$ ratio for the solution in equilibrium with both $Al_2O_3,2SeO_3,11H_2O$ and $Al_2(SO_4)_3,16H_2O$ can be taken to be about 2·9. This means in practice that a solution prepared so as to have an $SeO_3/Al_2O_3$ ratio of 2·7 should be able to yield on crystallisation at 25° approximately 3 parts by weight of pure $Al_2O_3,2SeO_3,11H_2O$ and 9 parts of mother-liquor before $Al_2(SeO_4)_3,16H_2O$ would begin to separate [Found, for a preparation from aluminium hydroxide and selenic acid: $Al_2O_3$, 18·51; $SeO_3$, 45·99 (Se, 28·62). Found, for a preparation from aluminium *iso*propoxide and selenic acid: $Al_2O_3$, 18·37; $SeO_3$, 46·15 (Se, 28·71)%].

$5Al_2O_3,6SeO_3,40H_2O$. The first crop of crystals obtained during one preparation of $Al_2O_3,2SeO_3,11H_2O$ from aluminium hydroxide and selenic acid gave figures on analysis which indicated a mixture in roughly equal proportions of $Al_2O_3,2SeO_3,11H_2O$ and $5Al_2O_3,6SeO_3,xH_2O$.

3·46 G. of the mixture were stirred with 25 c.c. of approximately 2% selenic acid for a short time, and the solid collected on a small Buchner funnel and washed with alcohol of increasing concentration. The washed crystals after air-drying weighed 0·842 g. and consisted of aggregates of minute prisms showing straight extinction in some positions and looking very like some preparations of $5Al_2O_3,6SO_3,xH_2O$ [Found: $Al_2O_3$, 25·54; $SeO_3$, 39·17 (Se, 24·36); $Al_2O_3/SeO_3 = 0{\cdot}812$. $5Al_2O_3,6SeO_3,40H_2O$ requires $Al_2O_3$, 25·61; $SeO_3$, 38·25 (Se, 23·80)%; $Al_2O_3/SeO_3 = 0{\cdot}833$]. The *compound* was reasonably pure, the value of $Al_2O_3/SeO_3$, being very similar to that of the corresponding ratio usually found for washed and air-dried preparations of the analogous basic sulphate (see Bassett and Goodwin, *loc. cit.*, pp. 2248, 2250).

*Selenate Analogues of the Alunites.*—Selenate alunites can be formed under similar conditions to those which lead to the formation of the sulphate alunites. We have only prepared the sodium salt, but it is evident that isomorphous mixtures are formed as in the case of the ordinary alunites (Bassett and Goodwin, *loc. cit.*, p. 2255), so the composition may differ considerably from that required by the conventional formula $M^{\cdot}[Al_3(OH)_6][SeO_4]_2$.

Sodium hydroxide solution was added gradually to some aluminium selenate mother-liquors containing about 5 g. of $Al_2(SeO_4)_3,16H_2O$. A copious precipitate was produced, and as the mixture had become alkaline sufficient selenic acid was stirred in to make it markedly acid. The mixture—about 35 c.c.—was heated for a fortnight with occasional stirring at 70—90°. The precipitate settled well but was too fine for any crystalline form or double refraction to be detected under the microscope. It was filtered off on the pump on a hardened filter-paper, well washed with cold water, and air-dried to constant weight; yield 1·7 g. The mother-liquor had a pH of about 1. For analysis the solid was dissolved (fairly easily) by digestion with the minimum amount of concentrated sulphuric acid diluted with an equal volume of water [Found: $Na_2O$, 6·05; $Al_2O_3$, 29·33; $SeO_3$, 52·36; $H_2O$ (by diff.), 12·26%]. This composition agrees well with that calculated for the mixture of alunites shown below.

| Compound. | $Na_2O$, %. | $Al_2O_3$, %. | $SeO_3$, %. | $H_2O$, %. | Total, %. |
|---|---|---|---|---|---|
| $Na[Al_3(OH)_6][SeO_4]_2$ | 4·70 | 23·22 | 38·54 | 8·20 | 74·66 |
| $Na[Al_2(OH)_3(H_2O)_3][SeO_2]_4$ | 1·35 | 4·43 | 11·03 | 3·52 | 20·33 |
| $H_2O[Al_3(OH)_5H_2O][SeO_4]_2$ | — | 1·68 | 2·79 | 0·89 | 5·36 |
| | 6·05 | 29·33 | 52·36 | 12·61 | 100·35 |

$Na_2SeO_4,Al_2(SeO_4)_3,22H_2O$ [$= NaAl(SeO_4)_2,11H_2O$]. According to Meyer and Speich (*Z. anorg. Chem.*, 1921, **118**, 14), $Al_2(SeO_4)_3,18H_2O$ [*i.e.*, $Al_2(SeO_4)_3,16H_2O$] can be obtained by double decomposition between aluminium chloride and sodium selenate in presence of much acetic acid. We were unable to get this result by following the method as closely as possible but obtained the double *salt* $Na_2SeO_4,Al_2(SeO_4)_3,22H_2O$ in 90% yield, calculated on the sodium selenate used. The crystals which have separated rapidly from solution tend to form somewhat elongated six-sided plates with all angles 120°. These crystals look very like the thin plates of $Al_2(SeO_4)_3,16H_2O$ but are considerably thicker. On slow crystallisation from aqueous solution, stout, almost square crystals separate which have a high refractive index and are strongly doubly refracting. Either two opposite angles of the plates or all four of them are often truncated. The six-sided plates and the almost square crystals have the same composition [Found, after air-drying and alcohol washing: $Na_2O$, 5·86; $Al_2O_3$, 9·57; $SeO_3$, 47·46 (Se, 29·52). $NaAl(SeO_4)_2,11H_2O$ requires $Na_2O$, 5·81; $Al_2O_3$, 9·55; $SeO_3$, 47·57 (Se, 29·59)%]. Meyer and Speich's identification of the compound as $Al_2(SeO_4)_3,18H_2O$ depended merely upon an aluminium determination on vacuum-dried material. On further evaporation, isotropic crystals of sodium chloride eventually separate from the mother-liquor of the double selenate. The crystallographic characteristics of the double selenate are similar to those given by Soret (*Arch. Sci. Genève*, 1884, **11**, 62; 1885, **13**, 9) for the corresponding double sulphate, *viz.*, $Na_2SO_4,Al_2(SO_4)_3,23H_2O$, but Surgunoff (*Bull. Acad. St. Petersburg*, 1909, **3**, 1057) showed that only $22H_2O$ were present. We obtained this compound several years ago but in the meantime its preparation by direct combination of sodium and aluminium selenates has been described by Collet (*loc. cit.*) but without supporting analysis.

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