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# CONTRIBUTIONS TO THE CHEMISTRY OF SELENIUM AND SELENIUM COMPOUNDS—V*
## THE HYDROLYSIS OF SELENIUM

E. SCHULEK and E. KÖRÖS
Institute of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest

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**Abstract**—The reactions of selenium with water, with alkali hydroxides and with ammonium hydroxides were investigated. The reactions of selenium with alkali hydroxides and ammonium hydroxide afford colloidal selenium solutions. The experimental evidence was supported by theoretical considerations, on the basis of redox potentials.

IN one of our earlier communications⁽¹⁾ we discussed in detail the hydrolysis of sulphur. The reaction between sulphur and water primarily yields hydrogen sulphide and sulphoxylic acid whilst primarily polysulphide and thiosulphate form in the reaction between sulphur and alkali hydroxides. However, this polysulphide is only an intermediate and, in the further course of hydrolysis, disproportionates into hydrogen sulphide and thiosulphate.

It seemed to be of interest to examine whether a similar hydrolysis also occurs with selenium, and to determine which products form in the reactions between selenium and water, alkali hydroxide and ammonium hydroxide, respectively.

This problem has been relatively rarely discussed in the literature and the statements are rather contradictory.

According to SCHULZE,⁽²⁾ red selenium is soluble in water whilst in the investigations by JANNEK and MAYER,⁽³⁾ amorphous selenium proved to be completely insoluble in water. Reaction to a slight extent has been observed at 160° by CROSS and HIGGIN.⁽⁴⁾ In the opinion of MONTAGNIE,⁽⁵⁾ freshly precipitated red selenium probably reacts with water over 50° as follows:

$$Se + 2H_2O = SeO_2 + 2H_2 \qquad (1)$$

Grey selenium was not attacked by water at 160°.

BERZELIUS⁽⁶⁾ was the first to study the reactions between selenium and alkali hydroxides and observed that on boiling selenium and concentrated potassium hydroxide, a dark brown solution of potassium selenide was formed. On investigating the rate of reaction between potassium hydroxide and selenium, ESPIL⁽⁷⁾ established the following equation:

$$6KOH + (2n + 1)\,Se = 2K_2Se_n + K_2SeO_3 + 3H_2O \qquad (2)$$

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* Part I: *Z. Anal. Chem.* **139**, 20 (1953); Parts II, III, IV: *Talanta* **3**, 23, 27, 31 (1959).

(1) E. SCHULEK, E. KÖRÖS and L. MAROS, *Acta Chim. Hung.* **10**, 291 (1956).

(2) H. SCHULZE, *J. Prakt. Chem.* **32**, 390 (1885).

(3) J. JANNEK and J. MEYER: *Z. Anorg. Chem.* **83**, 69 (1913).

(4) C. F. CROSS and A. HIGGIN: *J. Chem. Soc.* **35**, 249 (1879).

(5) E. MONTAGNIE, *Bull. Soc. Chim. Fr.* (5) **1**, 507 (1934).

(6) J. J. BERZELIUS, *Lehrbuch der Chemie* (3rd Ed.), Vol. 3, p. 26. Dresden-Leipzig (1834).

(7) R. L. ESPIL, *Bull. Soc. Chim. Fr.* (4) **7**, 155 (1910).

The same results were also obtained by CALCAGNI.(8) The problem was most thoroughly examined by ADAMI.(9) According to his investigations, which will critically be discussed by us later, the reaction of sodium hydroxide and selenium affords selenide, selenite and selenoselenate $Se_2O_3^{2-}$.

According to BERZELIUS(6) and GORE,(10) no reaction takes place between selenium and ammonium hydroxide whilst CALCAGNI(8) observed that selenium dissolves to a minute extent.

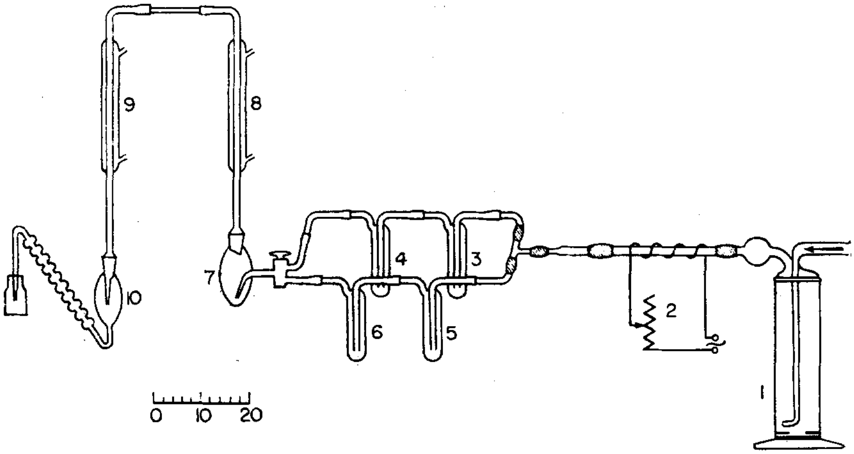

FIG. 1.

## EXPERIMENTAL

### 1. *Reaction of selenium and water*

The only equation known for the reaction between selenium and water originates from MONTAGNIE.(5) It does not seem probable that selenium would be capable of producing hydrogen from water at the low temperature applied. On repeating these experiments, we used a gas buret to collect any hydrogen formed on heating. Our experiments with amorphous selenium, crystalline red selenium and grey selenium proved that, in the absence of oxygen, selenium does not react with water at 100°C. We did not detect any of the reaction products suggested by MONTAGNIE. However, in the presence of air, boiling amorphous selenium with water yielded minute quantities of selenous acid.

It was rather difficult to study the hydrolysis, since amorphous selenium of high reactivity quickly converts into grey selenium at 100°. Accordingly, the reaction, if it existed at all, would soon come to an end. Therefore, it seemed necessary to "stabilize" red selenium in a satisfactory way. For this purpose, we prepared first selenosulphide $(SSe_x)^{2-}$ from sodium sulphide and selenium, since loosely bound selenium does not quickly convert into grey selenium on boiling. On boiling the solution for several hours in a nitrogen current, the presence of selenium was detected in the absorption tube which served as receiver.

### 2. *The reaction of selenium and alkali hydroxides*

The apparatus shown in Fig. 1. was connected with a cylinder of nitrogen. Traces of oxygen were removed from the gas by traps (1) and (2) containing an alkaline solution of ditionite in pyrogallol and manganese (II) oxide(11) respectively. Trap (3) remained empty whilst 10 ml of a 2 per cent solution of potassium cyanide was placed in trap (4), and traps (5) and (6) each contained 10–15 ml of water.

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(8) G. CALCAGNI, *Gazz. Chim. Ital.* **53**, 114 (1923).

(9) P. ADAMI, *Atti Mem. R. Acad. Sci. Lettere Arti Padova, Mem. Cl. Sci. fisico-mat.* **51**, 13 (1934/35).

(10) G. GORE, *Proc. Roy. Soc.* **20**, 441 (1872).

(11) E. SCHULEK and E. PUNGOR, *Mikrochim. Acta* **7–8**, 1116 (1956).

These traps were connected with the reactor flask (7) which contained the weighed sample of selenium (ca. 0·1 g) and some solid sodium or potassium hydroxide (ca. 2 g) in a glass flask which was easily inverted. Two condensers (8, 9) and a ten-ball absorption tube filled with dilute sodium hydroxide (01) were attached to the reactor flask.

A nitrogen current was passed through the apparatus for 30 min, in order to remove air, and then water was introduced into the reactor flask by turning over tiap (6). On boiling the reaction mixture for several minutes, selenium completely dissolved, yielding a dark red solution. On allowing this solution to cool in a nitrogen current, trap (4) was inverted, and the solution of potassium cyanide added to the reactor flask (7).†

TABLE 1

| Alkalihydroxide | Weighed Se (mg) | Consumed ml of 0·01 N $Na_2S_2O_3$ |  | Found mg of Se/100 ml |  |
|---|---|---|---|---|---|
|  |  | for $Se^0$* | for $Se^{+IV}$* | $Se^0$ | $Se^{+IV}$ |
| NaOH<br>(ca. 2 g) | 120·4 | 6·08<br>6·08 6·07<br>6·05 | 0·10<br>0·13 0·12<br>0·12 | 119·8$_2$ | 0·24 |
| KOH<br>(ca. 2 g) | 110·0 | 5·56<br>5·54 5·55<br>5·55 | 0·09<br>0·06 0·07<br>0·05 | 109·5$_6$ | 0·14 |

* From the solution diluted to 100 ml 2·00 ml was taken out for $Se^0$ determination and 10·00 ml for $Se^{+IV}$ determination.

The reaction took place instantaneously and the solution became colourless. The contents of the reactor flask were transferred into a 100 ml measuring flask and made up to volume with distilled water previously boiled and cooled. The analysis was carried out as follows;

*Estimation of* $Se^0$(12). To an aliquot portion of the solution 0·5 g boric acid was added and it was diluted to 60–70 ml. The solution was boiled for 10 min to expel the excess of cyanide and after cooling the pH was adjusted to 3·5–4·0 with dilute perchloric acid. Bromine water was added to the solution to give a permanent yellow colour and the excess of bromine was taken up with 5 ml of 5 per cent phenol. 2 ml of 20 per cent perchloric acid and 0·1 g of potassium iodide were added and after 20 min the iodine was titrated with 0·01 N sodium thiosulphate-solution.

*Estimation of* $Se^{+IV}(SeO_3^{2-})$. To another aliquot portion of the solution solid potassium hydrogen carbonate, 10 ml of conc. hydrochloric acid and 2 g of potassium iodide were added. Iodine was measured with 0·01 N sodium thiosulphate solution.

*Estimation of* $Se^{-II}(Se^{2-})$. Another aliquot portion of the solution was pipetted into a distillation flask and 10 ml of 2 N sulphuric acid were added to it. The solution was boiled for 15 min and dilute sodium hydroxide solution was used for the absorption of hydrogen selenide. No traces of selenide were found.

The results are summarized in Tables 1 and 2.

The reaction of selenide and selenite was studied in detail. Sodium selenide was prepared by the absorption by sodium hydroxide of hydrogen selenide formed by the hydrolysis of aluminium selenide. The solution obtained was poured on to sodium selenite in an apparatus free from oxygen (sodium selenite was in a small excess). The analysis of the resulting red solution proved only the presence of elementary selenium and the excess of selenite.

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† The reaction should be carried out in a nitrogen current because selenium of a high degree of dispersity quickly oxidizes in air. However, selenocyanide is not attacked by molecular oxygen.

(12) E. SCHULEK and E. KÖRÖS, *Z. Anal. Chem.* **139**, 20 (1953).

### 3. *Reaction of selenium and ammonium hydroxide*

The experiments were carried out with (a) amorphous red selenium, (b) crystalline red selenium and (c) grey selenium.

Samples of 100–150 mg of selenium and about 3 ml of concentrated ammonium hydroxide solution were transferred into sealed tubes of about 4·0–4·2 ml volume. The introduction of these substances completely removed air from the tube. After sealing the open ends of the tubes, they were heated in a furnace to 240° and kept at this temperature for 1 hr. The tubes were examined on cooling. In the cases (a) and (b), the solution turned slightly red whilst in case (c) it remained colourless.

After opening the tubes, 1–2 ml of 2 per cent potassium cyanide was added to the solutions. The unreacted grey selenium was filtered off and the solution was transferred to a 100 ml volumetric flask.

The estimation and detection of $Se^0$, $Se^{+IV}$ and $Se^{-II}$, respectively, were carried out as described above. Some tenth of a mg of $Se^0$—as a colloidal solution—was found in the tubes. Neither $Se^{+IV}$, nor $Se^{-II}$ could be detected.

TABLE 2

| Alkali hydroxide | Selenium compound formed (%) | | |
|---|---|---|---|
| | $Se^{-II}$ | $Se^0$ | $Se^{+IV}$* |
| NaOH | 0 | 99·8 | 0·2 |
| KOH | 0 | 99·9 | 0·1 |

* The presence of some tenth per cent of selenite is probably due to traces of oxygen which entered the system. On carrying out the reaction in air, the reaction mixture contained 92–93 per cent of $Se^0$ and 8–7 per cent of $Se^{+IV}$, no $Se^{-II}$ being detectable.

## DISCUSSION

### 1. *Reaction of selenium and water*

According to our experiments selenium reacts with water only to a small extent and therefore the exact identification of the selenium compound causes great difficulties.

It seems possible, however, that the compound distilling is hydrogen selenide and the hydrolysis of selenium can be written:

$$3Se + 3H_2O \rightleftharpoons 2H_2Se + H_2SeO_3 \qquad (3)$$

Results obtained for the alkali hydrolysis of selenium support this assumption. (See below.)

### 2. *Reaction of selenium with alkali hydroxides*

It appears from the previously given survey of the literature that the dissolving of selenium in alkali hydroxides is considered to be analogous to the dissolving of sulphur. However, with the exception of ADAMI, the method of analysis of the reaction products is not given by the authors.

According to ADAMI,(9) 96·18 per cent of polyselenide, 3·77 per cent of selenite and 0·45 per cent of selenoselenate ($Se_2O_3^{2-}$) form, in the sense of the reaction schemes:

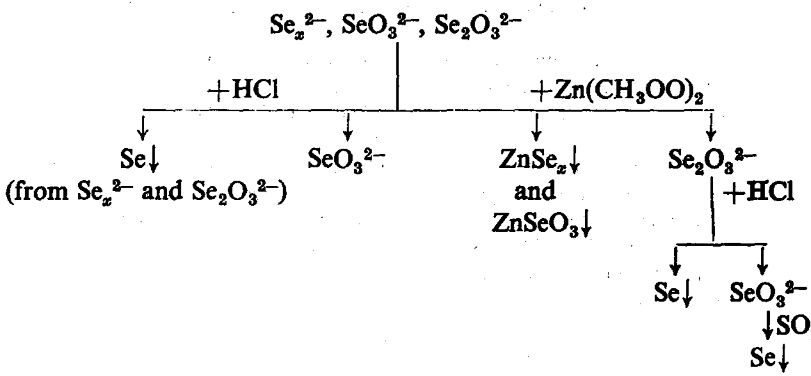
$$2Se + 2H_2O \rightleftharpoons Se^{2-} + SeO_2^{2-} + 4H^+ \qquad (4a)$$

$$3SeO_2^{2-} = Se^{2-} + 2SeO_3^{2-} \qquad (4b)$$

$$Se^{2-} + nSe = Se_{n+1}^{2-} \qquad (4c)$$

$$SeO_3^{2-} + Se \rightleftharpoons Se_2O_3^{2-} \qquad (4d)$$

The analysis method used by Adami may be presented schematically:



However, there are some errors in the course of the analysis followed by Adami.

1. On acidifying, not only elementary selenium but also hydrogen selenide should form from polyselenide. Hydrogen selenide is not mentioned at all by Adami.

2. The course of analysis given by Adami does not unequivocally prove the existence of the presumed selenoselenate /$Se_2O_3^{2-}$/*. Thus, selenite and polyselenide may not be precipitated quantitatively by zinc acetate, and the precipitation of selenium on subsequent acidification may be explained in this way.

3. The dissolving of selenium by alkali hydroxides is a disproportionation in the true sense, and identical quantities of oxidation and reduction products should form. However, the analytical data of Adami disclose that either the reduction products are in excess or the ratio $Se_x/Se^{2-}$ has a value of 88·6/7·6 = 11·7 which seems to be quite improbable.

4. It must be noted as well that the polyselenideselenium forms in the reaction in a highly dispersed state and is readily oxidized by atmospheric oxygen. Consequently, conclusions as regards the course of the reaction can only be drawn from experiments conducted in a medium completely free of oxygen.

The course of the reaction between selenium and alkali hydroxide or ammonium hydroxide (this latter reacts only at high temperature and pressure) is presumably as follows. Selenium reacts with hydroxyl ions to afford selenide and selenite:

$$3Se + 6OH^- \rightleftharpoons 2Se^{2-} + SeO_3^{2-} + 3H_2O \qquad (5)$$

Selenide and selenite immediately react with each other, with the formation of colloidal red selenium. Our analytical results proved that red selenium in a highly disperse form is the sole product of these reactions. The assumption that both selenide and selenite occur in the end products of the reaction seems incorrect. It is important to note that under the conditions investigated by us ($t_{max} = 240°$, $p_{max} = 30$ atm) grey selenium did not react with ammonium hydroxide.

On carrying out the reaction with barium hydroxide the process described by equation (5) is not completely shifted in the sense of the lower arrow, due to the slight solubility of barium selenite, and the presense of selenide could be detected.

$$3Ba(OH)_2 + (2x + 1)Se = BaSeO_3 + 2BaSe_x + 3H_2O \qquad (6)$$

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* Selenoselenate is called hyposelenite by Adami; our efforts to prepare sodiumselenoselenate from sodiumselenite and selenium were unsuccessful.

This interpretation of the reaction can be supported by a knowledge of the redox potentials.

Considering the redox potentials of the partial reactions:

$$\mathrm{Se^{2-} = Se + 2}e \qquad E_0 = -0{\cdot}92\ \mathrm{V}^{(13)}$$

and,

$$\mathrm{Se + 6OH^- = SeO_3{}^{2-} + 3H_2O + 4}e \qquad E_0 = -0{\cdot}37\ \mathrm{V}^{(13)}$$

then, combining both equations:

$$\mathrm{2Se^{2-} + SeO_3{}^{2-} + 3H_2O = 3Se + 6OH^-}$$

$$K = \frac{[\mathrm{Se}]^3\,[\mathrm{OH^-}]^6}{[\mathrm{Se^{2-}}]^2\,[\mathrm{SeO_3{}^{2-}}]}$$

Taking the concentrations of selenium and of hydroxyl ions equal to unity,

$$K = \frac{1}{[\mathrm{Se^{2-}}]^2\,[\mathrm{SeO_3{}^{2-}}]}$$

$$E_{0_{\mathrm{SeO_3{}^{2-}}}} + 0{\cdot}015 \log \frac{1}{[\mathrm{Se^{2-}}]^2} = E_{0_{\mathrm{Se^{2-}}}} + 0{\cdot}015 \log\,[\mathrm{SeO_3{}^{2-}}]$$

from this

$$[\mathrm{Se^{2-}}]^2\,[\mathrm{SeO_3{}^{2-}}] = 10^{-36.6}$$

Thus, equation (5) completely shifts in the direction of the lower arrow.

It is of interest to compare the reactions of sulphur and of selenium, respectively, with alkali hydroxides and ammonium hydroxide:

(a) when sulphur is dissolved by alkali hydroxides and by ammonium hydroxide, the primarily formed sulphoxylate or sulphite quickly converts into thiosulphate. In contrast to that, selenite is not capable of further conversion;

(b) in an alkaline solution, sulphide is not oxidized by sulphite whilst selenide is oxidized by selenite, giving the precipitation of elementary selenium. Consequently, the hydrolysis of sulphur and selenium in alkaline solutions are not analogous reactions.

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(13) M. M. LATIMER, *The Oxidation States of the Elements* pp. 82–83. McGraw-Hill, New York (1946).