CXXX.—*The Oxidation Potential of the System Selenium Dioxide–Selenium.*

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SELENIUM dioxide is readily reduced to selenium and it appeared that a study of the oxidation potential of the system selenium dioxide–selenium would furnish interesting data for comparison with that of the analogue : sulphur dioxide–sulphur (Carter and James, J., 1924, **125**, 2231).

Preliminary *E.M.F.* measurements were carried out with various half-elements in combination with the calomel electrode. Each cell contained several platinum foil electrodes, some of which were plain and others platinised. The solid selenium used in cells 2, 3 and 5 was the red amorphous variety. In some cases, the platinum foil was buried in the selenium, whilst in others the selenium was deposited electrolytically.

Cell 1. (Pt)|0·1*M*-SeO_2, 0·1 *M*-Na_2SeO_4, H_2O
2. (Pt)|0·1*M*-SeO_2, Se (solid), H_2O
3. (Pt)|0·1*M*-SeO_2, Se (solid), 10*N*-HCl
4. (Pt)|0·1*M*-SeO_2, Se (in solution), 10*N*-HCl
5. (Pt)|Se (solid), 10*N*-HCl

1 and 2 gave ill-defined potentials and they were greatly affected by polarisation. 3 and 4 gave well-defined potentials. In 5, the potential was ill-defined, but on the addition of selenium dioxide it rose several tenths of a volt and became steady.

From these and subsequent experiments it was concluded that a definite potential was exhibited, provided that the solution were strongly acid and that selenium dioxide and selenium were each present in solution. In the case of the selenium, it might be present in quantity to form either a saturated or an unsaturated solution. In this connexion, the solubility of selenium is important and experiment revealed the following facts :

1. Red amorphous selenium was stirred with concentrated hydrochloric acid at 20° for 3 days, but no selenium was dissolved. Moreover, under these conditions no selenium dioxide was formed, although the solution was in contact with air.

2. Selenium is soluble in concentrated hydrochloric acid in presence of selenium dioxide. The solubility of selenium in 0·1*M*-SeO_2 and 11·6*N*-HCl is 1·35 g. per litre (within 5%).

3. The solubility of selenium falls off rapidly with diminishing concentration of acid, and, on dilution of saturated solutions with water, the red amorphous selenium is precipitated.

It was therefore decided to determine the oxidation potential of the system selenium–selenium dioxide–concentrated hydrochloric acid, and to study the influence of changes in concentration of (*a*) selenium, (*b*) selenium dioxide.

In order to obtain reproducible values of the *E.M.F.* it was obvious that the quantity of dissolved selenium would have to be carefully controlled.

Materials.—Selenium dioxide was prepared by dissolving amorphous selenium (B.D.H.) in concentrated nitric acid and evaporating the solution to dryness. The product was twice sublimed in small quantities in a large crucible and thereby freed from tellurium. Pure amorphous selenium was prepared from the purified selenium dioxide by passing sulphur dioxide through a slightly acid solution; after thorough washing on an asbestos pad, the precipitate was dried in a vacuum. The hydrochloric acid employed throughout was B.D.H., As.T. quality.

Preparation of Solutions.—A solution of selenium in concentrated hydrochloric acid containing selenium dioxide was prepared by shaking amorphous selenium with the liquid for several days. The clear solution (deep amber colour) was withdrawn into a pipette through a pad of glass wool and portions were analysed. The stock solution had the following composition: $0{\cdot}066N\text{-}SeO_2$, $0{\cdot}0134N\text{-}Se$, $11{\cdot}6N\text{-}HCl$. This was used for making up the cell solutions by suitable dilution with hydrochloric acid of the same concentration and addition of the proper amounts of selenium dioxide either as the solid or from the stock solution. The composition of some of the solutions was checked by analysis.

Analysis.—The determination of selenium dioxide was based on that of Norris and Fay (Gooch, "Methods in Chemical Analysis," 1912, p. 383) for acid solutions. 10 C.c. of the concentrated acid solution are added to 300 c.c. of ice and water. 50 C.c. of $N/10$-sodium thiosulphate are then run in, the excess being titrated with standard iodine solution, starch paste being used as indicator. This method gave accurate results if the conditions were strictly observed.

The estimation of the amount of dissolved selenium was a more difficult matter. At first, the greater part of the hydrochloric acid was evaporated on the water-bath, and the selenium precipitated by the addition of water. This method gave variable results owing apparently to the volatilisation of a portion of the selenium. The method finally adopted was to dilute 100 c.c. of the solution with a litre of water. The selenium separated in a very finely-divided form which did not settle readily. On adding a few c.c. of a strong solution of potassium chloride, however, the precipitate rapidly settled in a compact curdy form, which was filtered off through a Gooch crucible, dried at 110°, and weighed. Long heating at this temperature caused no loss of weight by volatilisation. The filtrate showed no sign of containing any free selenium. It was colourless and clear, and no perceptible turbidity appeared on further dilution.

Hydrochloric acid was determined in a separate portion by suitable dilution and titration with standard sodium carbonate.

Electrical Measurements.—It was feared that the presence of concentrated hydrochloric acid in one half of the cell would give rise to a troublesome liquid boundary and make accurate measurements impossible.

The following type of cell was finally found to be most suitable for the purpose:

$$(\mathrm{Pt})\left|\begin{array}{l} yN\text{-}\mathrm{SeO_2} + zN\text{-}\mathrm{Se} \\ 11{\cdot}6\ N\text{-}\mathrm{HCl} \end{array}\right.\underbrace{\Big|\ N\text{-}\mathrm{HCl}}_{\substack{\text{Stationary}\\ \text{junction.}}}\underbrace{\Big|\ \mathrm{KCl}}_{\substack{\text{Flowing}\\ \text{junction.}}}\ (\text{sat.})\left|\begin{array}{l} \mathrm{Hg_2Cl_2} \\ \mathrm{KCl}\ (\text{sat.}) \end{array}\right|\mathrm{Hg}$$

This arrangement gave reproducible results and was not liable to fluctuations of more than a few tenths of a millivolt during the experiments. Moreover the boundary potentials are of types which may be evaluated if required.

A stationary junction being used at the N-HCl|KCl (sat.) boundary, variations of 0·0025 volt over a 10-minute range were experienced, whilst, with the flowing junction, readings constant to 0·0001 volt during 15 minutes were obtained. This is of interest, since the flowing junction has hitherto been applied to junctions of the type HCl|KCl for concentrations of 0·1N and N (Lamb and Larson, *J. Amer. Chem. Soc.*, 1920, **42**, 229). The present work shows how it may be employed advantageously in connecting a saturated potassium chloride solution with highly concentrated acid.

The electrodes were of platinum platinised in the usual way. A fresh electrode took some time to acquire a definite potential, but electrodes that had been immersed in one of the solutions, after being washed once or twice with a fresh solution, rapidly assumed a steady potential. In some preliminary experiments a metre bridge in conjunction with a capillary electrometer was employed. With this arrangement, it was found that the electrodes, particularly in the more dilute solutions, were very readily polarised, even with the small currents which passed in finding the balance point, and took some time to recover the original potential. In the later work a Cambridge ionisation potentiometer was used, giving readings direct to 0·2 millivolt with a sensitive A. M. galvanometer. No trouble was experienced with this arrangement on account of polarisation.

Three electrodes were placed in the electrode vessel. After use in a few cells an electrode often became irregular and differed from the other two. Fairly frequent replatinising was necessary. The electrode vessel was kept in a thermostat at 20° ± 0·1° during the measurements. The saturated calomel electrode was one of a battery of four which were frequently compared and at no time differed by more than 0·25 millivolt. The calomel electrodes were at room temperature. This was determined exactly by a thermometer in the liquid of one of them, at the time of every measurement, and the correction introduced.

Reproducibility and Constancy.—Although with the more concentrated solutions the mean potentials were easily reproduced to within a fraction of a millivolt (*e.g.*, cell D), minor fluctuations, usually less than a millivolt, were sometimes observed. On the other hand, the solutions containing the more minute concentrations of selenium exhibited a gradual drift in the potential. This was most apparent in cell C, where a gradual decrease from 0·5452 to 0·5247 volt at 12° over a period of 22 hours was observed. This was not due to changes in the immediate vicinity of the electrodes, for only a minute alteration of the potential occurred on shaking the cell. The drift appeared to be due to some decomposition in the cell, which was accelerated by the higher temperature of the thermostat, this being slightly above that of the room. A portion of the solution C, which had remained at room temperature for 24 hours, gave a slightly lower potential than the original reading; when placed in the electrode vessel in the thermostat, its rate of drift was greater. It appeared that the reaction concerned was the reduction of selenium dioxide by hydrochloric acid: $SeO_2 + 4HCl = Se + 2H_2O + 2Cl_2$.

The formation of selenium to only a slight extent in this reaction would have an appreciable effect on the selenium concentration at the minute concentrations of the more dilute cells. This supposition was supported by the fact that a stock solution of selenium dioxide in concentrated hydrochloric acid, kept at room temperature, acquired after some days a faint yellow tint. The potential of a platinum electrode in this solution measured against the saturated calomel electrode was 0·614 volt, which would correspond to a selenium concentration of about $10^{-5}M$.

Measurements.—A typical set of potentiometer readings is in Table I, which gives the observations for three freshly prepared cells, D1, D2 and D3, respectively. (The selenium electrode is positive with respect to the calomel.)

E (*t*°) is the observed *E.M.F.* when the oxidation cell is at 20° and the calomel electrode is at room temperature, *t*° : *E* (20°) is the *E.M.F.* after correcting the calomel electrode to 20°.

TABLE I.

$[SeO_2]$ = 0·0866, [Se] = 0·00134, [HCl] = 11·6.

Cell.	Hrs.	Mins.	*E*(*t*°) observed.			*E*(*t*°) mean.	*E* (20°).
D. 1.		10	0·5738	0·5739	0·5736	0·5733 *t* = 13·5°	0·5720
	1	20	0·5732	0·5732	0·5730		
	3	20	0·5729	(0·5716)	0·5728		
D. 2.		10	0·5733	0·5733		0·5734 *t* = 13·0°	0·5720
		40	0·5742	0·5743			
	1	5	0·5728	0·5728			
	3	5	0·5718	0·5718			
	20	0	0·5678	0·5678			
D. 3.	0	40	0·5734	0·5735		0·5729 *t* = 14·5°	0·5718
	1	35	0·5726	0·5726			
	2	30	0·5726	0·5726			
	5	40	0·5708	0·5708			

Similar determinations were made with solutions of different concentrations and the results are in Table II.

TABLE II.

[HCl] = 11·6*N*.

Cell.	$[SeO_2]$.	[Se].	*E* (20°).	Δ*E*.
A_1	0·087	0·0134	+0·5501	—
A_2	0·087	0·0134	0·5498	0·0222
D	0·087	0·00134	0·5720	0·0250
E	0·087	0·000134	0·5970	
B	0·0087	0·00134	0·5460	0·0260
F	0·0087	0·000134	0·5720	
C	0·00087	0·000134	0·5436	—

In Cell A_1, the junction *N*-HCl\|KCl (sat.) is stationary, but in A_2 and all the other cells the flowing junction was used.

The Influence of Concentration of Selenium Dioxide and of Selenium on Oxidation Potential.

(*a*) *Selenium.*—Table II gives this relation, since in Cells A_2, D and E the $[SeO_2]$ = 0·087 is constant and [Se] undergoes tenfold changes. Cells B and F afford a similar comparison. Δ*E* is the difference in *E.M.F.* for a tenfold change in [Se] and it amounts to 0·0222 to 0·0260 volt.

(*b*) *Selenium Dioxide.*—Table III gives this relation similarly, and it will be seen that Δ*E* for a tenfold change in $[SeO_2]$ varies from 0·0250 to 0·0284 volt.

TABLE III.

Cell.	$[SeO_2]$.	[Se].	*E* (20°).	Δ*E*.
D	0·087	0·00134	0·5720	0·0260
B	0·0087	0·00134	0·5460	
E	0·087	0·000134	0·5970	0·0250
F	0·0087	0·000134	0·5720	0·0284
C	0·00087	0·000134	0·5436	

Mechanism of the Oxidising Action of Selenium Dioxide and of Sulphur Dioxide.

The reduction of selenium dioxide in concentrated acid solution may conceivably proceed in a number of ways, of which the following may be considered.

1. The selenium dioxide dissolves in concentrated acid to form selenium tetrachloride, which ionises into quadrivalent selenium ions, $Se^{\cdot\cdot\cdot\cdot}$. On reduction, the four positive changes are removed and elementary selenium results :

$$SeO_2 + 4HCl \rightleftharpoons SeCl_4 + 2H_2O \rightleftharpoons Se^{\cdot\cdot\cdot\cdot} + 4Cl' + 2H_2O \rightleftharpoons Se + 4Cl' + 2H_2O + 4\oplus.$$

The potential variations, ΔE, would be given by $\Delta E = 0{\cdot}058/4 \,.\, \log [Se]/[SeO_2]$, and for a tenfold change in [Se] or in $[SeO_2]$, $\Delta E = 0{\cdot}058/4 = 0{\cdot}0145$ volt.

2. The reduction does not proceed entirely from the quadrivalent state down to elementary selenium, but only through certain intermediate stages, for example from quadrivalent to bivalent selenium. The essential portion of such a process may be represented

$$Se^{\cdot\cdot\cdot\cdot} = Se^{\cdot\cdot} + 2\oplus,$$

whence $\Delta E = 0{\cdot}058/2 \,.\, \log [Se^{\cdot\cdot}]/[Se^{\cdot\cdot\cdot\cdot}] = 0{\cdot}058/2 \,.\, \log [Se]/[SeO_2]$, and for a tenfold change in [Se] or in $[SeO_2]$, $\Delta E = 0{\cdot}058/2 = 0{\cdot}029$ volt.

Since part of the selenium dioxide is used in dissolving the selenium, the effective concentration is actually less than $[SeO_2]$ and a value somewhat smaller than 0·029 for ΔE will be obtained.

The existence of derivatives of bivalent selenium is indicated by the solubility of selenium in strong acid solutions containing selenium dioxide : $SeO_2 + Se = 2SeO$. In this connexion, it may be observed that selenium dissolves in selenic acid giving a green solution believed to contain Se_2O_3, an analogue of $SeSO_3$ which is formed by dissolving selenium in sulphuric acid (*Chem. News*, 1889, **59**, 268).

Either hypothesis depends on certain assumptions regarding the degree of ionisation and the unimolecular nature of the respective constituents in the equations. Experiments on these points are still proceeding. The experimental results for ΔE fall between those demanded by the two theories, but are rather in favour of the second.

The hypothesis that selenium acquires positive charges and behaves as an electropositive element is reasonable, since it has certain characteristics of a metal which are exhibited by its analogue tellurium, although scarcely at all by sulphur. Nevertheless the analogy with sulphur, even if only shown to a slight extent, is of interest in a study of the oxidising properties of sulphur dioxide and would furnish an explanation if sulphur could also become electropositive in acid solution (J., 1920, **117**, 1246).

Since negatively charged selenium ions Se″ or Se_n″ have already been identified in alkaline solutions, the present indication of positively charged selenium ions in acid solution furnishes additional evidence of the amphoteric nature of selenium (compare Le Blanc, Reichenstein, Müller, and Abegg; references, *Z. physikal. Chem.*, 1921, **97**, 257; 1922, **100**, 346).

The Effect of Light.—The potential of one of the oxidation cells, which had been kept in darkness, was not affected by sudden exposure to direct sunlight, or to the light of four filament lamps at a distance of a foot. On the other hand, bright metallic electrodes (made by melting selenium on platinum) in hydrochloric acid solutions of selenium dioxide and selenium gave a potential which was distinctly influenced by exposure to light. The selenium rapidly lost its brightness and the photosensitiveness disappeared. A selenium electrode made by the cathodic deposition of selenium on a selenium rod, and therefore covered with a layer of the amorphous kind, was quite unaffected by light.*

The photosensitiveness of the *E.M.F.* of selenium in aqueous solutions has been observed by Sabine and others (for references see C. Ries, "Das Selen," 1918, p. 188) and, although the significance of the presence of concentrated acid, selenium dioxide and dissolved selenium in determining the potential has not hitherto been emphasised, it is obviously of value in explaining the processes underlying many of their experiments.

These considerations are also useful in explaining the electrometric titration of selenium solutions by the bimetallic electrode system of Willard and Fenwick (*J. Amer. Chem. Soc.*, 1923, **45**, 933).

Summary.

The system selenium dioxide–selenium in concentrated hydrochloric acid gives a reproducible oxidation potential which has been measured.

The potential is unaffected by the action of light.

The influence of concentration of selenium and of selenium dioxide on potential has been studied, the changes for tenfold dilutions corresponding to 0·022—0·028 volt.

The oxidising action of selenium dioxide is provisionally attributed

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* We are indebted to Mr. W. F. Waters for some assistance in these experiments.

to the presence of selenium tetrachloride, which yields positively charged selenium ions.

The oxidising action of selenium dioxide and of its analogue, sulphur dioxide, are compared.

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