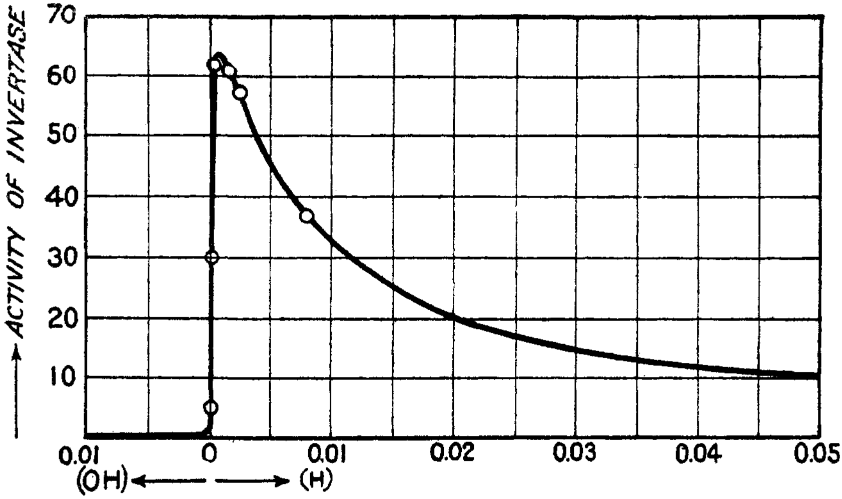
ties by the circles. On account of the rapid destruction of invertase at 30° by acid above 0.01 normal the relation can not well be tested beyond that concentration, but it is probable that at 0° such measurements can be made, and this will be attempted in the near future.



Graph of the formula for the activity of invertase.

The concentration of acid for which the enzymatic activity is a maximum can be calculated from equation (5). Writing its first differential with respect to $(\dot{H})$ equal to zero and solving gives

$$(\dot{H})_{\max} = \sqrt{\frac{K_1K_w}{K_2}}. \qquad (7)$$

Substituting in this the values previously found for these constants gives $(\dot{H})_{\max} = 0.8(10)^{-3}$ at 30°. Sörensen,[1] from his experiments at 52°, has found this value to be approximately $(10)^{-4}$; our results are thus in fair agreement with his, but they can not be strictly compared because of the different temperatures used, namely, 52° and 32°.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

METALLIC STRONTIUM.[2]

BY BEN L. GLASCOCK.

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In no case has strontium been obtained in sufficient amount to admit of a thorough study of its properties. The most complete investiga-

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[1] *Comptes rendus des travaux du Laboratoire de Carlsberg*, **8**, 132 (1909).

[2] From the author's doctoral thesis, 1909.

tion thus far has been that of Guntz and Roederer,[1] who prepared the metal from its hydride, made from the amalgam.

The purpose of the present investigation was to develop, if possible, a process or method by which the metal could be obtained in sufficiently large quantities to continue the study of its properties. The electrolysis of the fused chloride offered the most promising solution. It had been shown conclusively by Bunsen and Matthiessen and by Stockem and Borchers[2] that the metal could be made in this way. The problem resolved itself, then, into devising an improved or simpler form of apparatus, or a change in the electrical conditions.

The objection to the method of Bunsen and Matthiessen[3] is that with external heat, in addition to that afforded by the passage of the current, it is exceedingly difficult to regulate the temperature of the furnace so that a crust of chilled strontium chloride will always cover the bath in the inner cell. Stockem and Borchers avoided this difficulty by collecting the metal at the bottom of the bath. They found that the metal did not combine with the strontium chloride to such an extent as to render their method a failure. They cooled the bottom of the furnace, however, by means of a water jacket. The furnace of these workers is complicated, necessitating, as it does, the use of heavy insulation between the poles, a threaded point or rod for the cathode, and a water jacket for cooling purposes, all of which rendered the apparatus difficult of construction.

The method of Goodwin[4] for the preparation of calcium suggested itself as a possibility for strontium. To test it, a furnace was constructed by firmly binding together four Acheson graphite blocks by means of four heavy iron straps and bolts. The dimensions of the blocks were 10 cm. × 10 cm. × 30 cm. The two upper blocks had two semicircular sections sawed from them in such a way and of such a size that when they were fitted together they formed two holes 10 cm. deep, one 7.5 cm. in diameter, the other 10 cm. These holes fitted directly over depressions in the lower set of blocks, made by chipping out the graphite. Asbestos paper was put in between the blocks and the whole tightly bound together by means of the straps and bolts. The use of the asbestos was to prevent leaks, not to serve as insulation. The furnace was then connected to the + terminal of the feed wires by means of one of the bolts; thus all four blocks were connected with the current. An iron rod 2 cm. in diameter attached to the ratchet device used in the Goodwin furnace and connected to the — terminal served as the cathode. The circuit

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[1] *Compt. rend.*, **143**, 400–1.

[2] *Elec. Metallurgie*, Borchers, p. 84.

[3] *J. prakt. Chem.*, **107**, 253 (1869).

[4] THIS JOURNAL, **27**, 1403.

carried a 500-ampere ammeter and a 110-volt voltmeter, and a wooden barrel rheostat. The electrodes in the barrel were ordinary slabs of scrap iron, one of which could be lowered or raised by means of a cord passing over a pulley. If such a furnace would serve for the preparation of calcium it would be an improvement over the more or less fragile and complicated furnace of Goodwin, in that it could be taken apart entirely and the chilled calcium chloride left after the run easily removed, and in that it would do away with the use of the water-cooling apparatus, the graphite blocks being massive enough to conduct the heat away as rapidly as the water coil would, and also in that it would do away with the "gravity" cell of his furnace.

To try out the furnace, one of the holes was filled with melted calcium chloride, which had been fused in an iron dish in a wind furnace, the cathode lowered into the bath and the current switched on. Metallic calcium began at once to form on the iron, and rods of the metal as much as twenty inches in length were easily drawn out by means of the ratchet device. Each of the holes or furnaces were tried repeatedly. Each gave the same satisfactory results—they had equal efficiency. By repeated trials with varying current, it was found that about 80 amperes and 40–50 volts gave the best results with this apparatus. This, of course, is a matter that is entirely dependent upon the size and depth of the bath. The furnace, when full, contained enough calcium chloride to last six to eight hours with the above current, the yield in metal being in the neighborhood of 300 grams. As the object of these experiments was merely to show whether or not the furnace could be used successfully for calcium, no careful measurements or weights were taken with a view of ascertaining the efficiency of the apparatus. No inconvenience whatever was caused by leakage. Occasionally, however, a superficial lining of calcium fluoride was put into the furnace as an additional safeguard.

The Preparation of Metallic Strontium.

The apparatus described above was used with strontium chloride as the electrolyte, but metallic strontium was never obtained. It was impossible to prevent its burning and its combination with the electrolyte. It would not adhere to the cathode and thus become protected by a layer of strontium chloride, as is calcium in its preparation from calcium chloride. This may be due partly to the fact that it is less stable in the air than calcium is, and partly to the higher temperature of the electrolyte.

A cathode 6 cm. in diameter was substituted for the smaller one, and the current was just sufficient to keep the electrolyte molten. A layer of strontium chloride mixed with a small amount of metal was found to cover the end of the iron. A considerable quantity of hydrogen was evolved when the mixture was thrown into water. Three trials were made with this cathode with the same result.

A very small cathode, about 0.3 cm. in diameter, was next tried. The possibilities it held were that the intense heat in the immediate vicinity of the cathode would cause the liberated metal to fuse into globules and float, permitting their removal. After electrolyzing for 4–5 hours, with a current sufficient to keep the whole bath molten, the cathode was removed. No strontium was attached to it, nor were globules of the metal observed on the surface of the bath at any time during the operation. There seemed, however, to be less burning than usual. When the cold mass was broken open, it was found to be full of violet colored spots or nodules. These nodules gave considerable hydrogen when thrown into water. The experiment was repeated several times, but the results were never different.

It was thought perhaps metal could be obtained if the temperature of the electrolyte were lowered. For this purpose baths of strontium chloride with varying amounts of strontium fluoride were used. The cathode was the same as that used for calcium—2 cm. in diameter. When an electrolyte of strontium chloride and 10–20 per cent. of strontium fluoride with a current of 140–150 amperes and 20–30 volts was employed, globules of metal formed and floated about on the surface of the bath. Several of these were taken out, but they ignited at once, burning energetically with an intensely red flame. When the burning metal was thrown on the floor it broke into pieces and flew in all directions, tracing figures, as calcium or antimony does under similar conditions. When the cathode was removed, it was found to be covered with a layer of strontium chloride about 0.6 cm. in thickness, which contained so much metal that pieces of it glowed when struck violently with a hammer, and caused a brisk evolution of hydrogen when thrown into water. If a less powerful current was used, the metal burned as fast as it was formed, and if the current was allowed to fall after the metal began to separate, the globules were seen to glow and to gradually disappear.

When a bath of strontium chloride and about 50 per cent. of strontium fluoride with a current of 125 amperes and 40 volts was employed, it was noticed that small glowing particles were distributed through the mass, and they seemed to fall slowly to the bottom. Upon removing the cold material from the furnace, a thin black layer covered the bottom of it. It contained considerable metal and carbide.

This observation led to the next logical step—a reversal of the poles. This was done by placing a strip of sheet iron between the upper and lower sets of carbon, thus forming, at once, the cathode and the bottom of the furnace. A thick piece of asbestos with a hole in it to fit the furnace was laid over the iron and the whole apparatus bound together as before, after the upper set of blocks had been separated from the iron straps and bolts by thick pieces of asbestos. A carbon rod 2.5 cm. in diameter served as anode. In other words, the furnace of Stockem and Borchers had been arrived at, but in a much simplified form.

Using this furnace with the bath last described and a current of 20–30 amperes and 70–80 volts for three hours, a layer was formed on the cathode which contained considerable metal and carbide. The metal was not in globules. With a bath of strontium chloride and 25 per cent. of strontium fluoride and a current of 50–60 amperes and 50–60 volts for four hours a layer was obtained next to the cathode, which, in places, contained so much metal that when it was scratched, the whole took on a metallic luster. This, of course, soon disappeared because of the instability of the metal in air. It decomposed water energetically.

A bath consisting of strontium chloride and 10 per cent. of strontium fluoride was next used. The current was passed for $7^1/_2$ hours. About half the time it registered 150 amperes and 20 volts, the other half 60 amperes and 50 volts.[1] When the cold mass was broken open, it showed globules of metallic strontium. Many of the pieces were as large as a pea. Fourteen grams of the metal were separated. In addition to the metal several nodules of a brilliant yellow substance were found. This was very brittle, and was rather stable in the air; when put into water an energetic evolution of acetylene occurred.

The experiment was repeated, with like results.

An attempt was made to fuse together the pieces of metal that were too small to be separated mechanically. The residue was put into a 2.5 cm. gas pipe, capped at the ends, and placed in a vertical position in a wind furnace. The strontium alloyed with the iron and holes appeared in the cap and pipe, although the temperature was much below that of the melting point of iron.

The preceding experiences having demonstrated that any contrivance for cooling the furnace was unnecessary, it was decided to resort to an even simpler form of apparatus. To this end a cast iron vessel of hemispherical shape 25 cm. in diameter and walls 0.6 cm. in thickness was made to serve as a container. To keep the liberated metal from contact with the air and also to carry out Stockem and Borcher's idea of a small cathode, an iron rod 1.8 cm. in diameter, bent at right angles about two inches from its lower end, and this end then hammered to a blunt point, was made to serve as the cathode. A carbon rod 2.5 cm. in diameter was used as anode. By this arrangement, the current was made to pass entirely beneath the surface of the bath, since the vessel

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[1] During this electrolysis the carbons of the furnace attained a red heat throughout. This would indicate that a water jacket is entirely unnecessary, since the metal had been obtained under these conditions.

was deep enough to prevent the current passing to it and thence to the other electrode. It also admitted of the use of a porous cell arrangement—Bunsen and Matthiessen's idea.

The vessel was filled with fused strontium chloride, the current switched on, and a porous plate interposed. The same bath was used on three different days, connection being established by drawing an arc from the iron cathode upon the anode by means of a thin carbon rod held in the hand until the electrolyte was sufficiently fused to carry the current. During the electrolysis the bath in the vicinity of the cathode was always covered with a crust of chilled chloride. A very small amount of metal was seen to burn, but when the mass was broken up after the third day, only about 1 gram of metal was found.[1]

In the next experiment the dish was made to serve both as container and cathode, the anode remaining the same. Pure strontium chloride was used as the electrolyte. A current of 75 amperes and 75 volts was passed for $3^1/_2$ hours. Fifteen grams of metal were obtained. There was a noticeable decrease in the amount of carbide observed. The globules were larger than heretofore. The mass was re-fused and a current of 75 amperes and 75 volts passed for eight hours. Toward the end of the electrolysis, globules of metal were seen to come to the surface and float to the edge of the dish and either burn there or sink. Efforts to remove these globules were not very successful. When the bottom of the electrolyte was disturbed by scraping it with a rod, large pieces of metal would rise to the surface, showing the presence of considerable strontium.

It was thought that the metal could be made to run into one large piece, if the vessel and its contents were heated in a wind furnace. This was done. The strontium alloyed with the iron, however, produced a large hole in the bottom of the dish. The temperature was far below the melting point of iron. The iron in the vicinity of the hole was very soft, almost plastic, at low red heat. When cold it was hard and brittle, and had a different fracture from cast iron. A small amount of hydrogen was given off when it was boiled with water. Some of the metal was thoroughly washed, dissolved in hydrochloric acid, the solution filtered from the insoluble matter, and sulphuric acid and alcohol added to the filtrate. A heavy precipitate formed at once. Enough strontium was present to give a dense precipitate with sulphuric acid even in the absence of alcohol.

An iron mortar 15 cm. in diameter at the top and 15 cm. high, having

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[1] A very interesting observation was made at this point. When the residue was put into water, preparatory to recovering strontium chloride. a vigorous evolution of acetylene and ammonia took place. The odor of phenyl isocyanide was also detected. The greater portion of the carbon from the anode, however, remained as carbon when the residue was leached out with water.

a capacity of 1 liter, was substituted for the iron vessel just described. A current of 45 amperes and 75 volts for 8 hours gave about 7 grams of material which contained enough metal to render it malleable. Repeated trials failed to give any better results. The vessel was too small.

Another cast iron vessel of the same dimensions as the first one was procured. A carbon anode 8 cm. × 8 cm. was substituted for the smaller one. This large carbon permitted the use of a lower current density at the anode, thus reducing the temperature of the bath. With an electrolyte of pure strontium chloride and a current of 125 amperes and 40 volts for 7 hours, 76 grams of metallic strontium were obtained, giving a current efficiency of 5.3 per cent. One piece of the metal weighed 8 grams and several as much as 3 grams. This was the best yield obtained, but 30 to 50 grams were easily isolated by duplicating the above conditions. In all 360 grams of metallic strontium were made with this apparatus, which is extremely simple and involves the use of no expensive material. It was found that passing the current longer than 6–8 hours decreased the actual yield, the best percentage yield being when a current of 135 amperes and 35 volts was passed for only two hours. 29.5 grams of metal were isolated, or a current efficiency of 6.7 per cent. was attained.

Vessels and anodes of varying size and electrolytes of varying composition were tried out, but the conditions previously mentioned gave the best results.

The best method for separating the metal from the mixture consists in crushing it on an ordinary iron plate, then sieving out the metal.

Some very interesting phenomena and products revealed themselves during the process of recovering the strontium chloride from the melts. When the melt from the pure strontium chloride bath was extracted with water, there remained a residue which was soluble in hot water. Upon cooling this solution crystals separated. They had an alkaline reaction and all the properties of strontium hydroxide.

Upon concentrating the mother liquor from these crystals, it took on a pink color, which grew more intense as the concentration proceeded. The solution was alkaline. On addition of acid the color changed to light yellow. Bases restored the pink color. This product was obtained repeatedly, but never in amounts large enough to permit of the determination of its constitution.

To remove the iron salts from the first water extract, containing most of the strontium chloride, the solution was evaporated to dryness with a small amount of nitric acid and then baked, the residue extracted with water, and the extract made ammoniacal. The ammonium hydroxide instead of giving a red-brown precipitate of ferric hydroxide gave a voluminous white precipitate that resembled aluminium hydroxide.

Examination showed that it was neither an aluminium nor a titanium compound.

When the solution was evaporated to dryness without the addition of nitric acid, a blue tint would often appear around the edges of the residue, suggesting the presence of cyanide in the solution.

Properties of Metallic Strontium.

Strontium is a very light, soft metal of a silver luster when a new surface is first exposed; this, however, rapidly changes to a yellowish tint and finally to a white non-lustrous surface as the layer of oxide forms over it. It is harder than sodium but softer than calcium; it can be cut easily with a knife. It reacts with water, with methyl and ethyl alcohols, acetoacetic and malonic esters, and aniline with the evolution of hydrogen. It reacts slowly with ethyl iodide at the boiling point of the latter. It has no action upon silicon tetrachloride in either the hot or cold condition. It alloys with iron, and seems to combine with amorphous chromium and boron when heated with them. It dissolves very easily in liquid ammonia, giving a deep blue solution from which a dark blue precipitate separates as more metal dissolves. As the ammonia evaporates from this precipitate it passes through the beautiful play of colors that a clean sheet of copper shows as it cools after being heated to a high temperature, finally exhibiting a bright bronze luster and passing into a white compound as all the ammonia evaporates. Strontium burns in an atmosphere of carbon dioxide and illuminating gas as energetically as it does in air, but not so violently as calcium does under similar conditions. Carbon is set free and some carbide is formed when it burns in the former. Hydrogen and nitrogen unite with the heated metal when they are passed over it, forming the hydride and nitride, respectively. The hydride reacts more energetically with water and alcohol than the metal does.

On analysis three different samples of the metal gave the following results:

	I.	II.	III.
Insoluble	0.04	0.04	0.92
$Fe_2O_3(Al_2O_3)$	0.14	0.02	
Sr	97.11	98.50	98.54
Ca	...	...	None
Mg	...	...	None
Cl	1.75	...	...
O (by difference)	0.96	...	...
	100.00		

The specific gravity of strontium determined in dry toluene in a 50 cc. pycnometer gave the value 2.55.

The specific heat of the metal, determined in an ordinary water calorimeter, by putting a weighed amount of the metal into an ordinary test tube, covering it with a weighed quantity of dry toluene, and then the tube sealed off as near the surface of the liquid as possible, gave the following results after corrections had been made for the toluene and glass by means of a blank:

$$\left.\begin{array}{l}0.0779\\0.0701\\0.0736\\0.0757\\0.0771\\0.0681\\0.0768\end{array}\right\}\text{average, } 0.0742$$

This value multiplied by the atomic weight of strontium gives 6.5 as Dulong and Petit's constant.

Alloys.

Various alloys of strontium have been described. Willner[1] has made and analyzed alloys of strontium with tin, magnesium and aluminium.

An alloy of iron and strontium has not been mentioned in the literature. Such an alloy made in an accidental way has been noted in the first part of this communication. Hirsch and Aston[2] have shown that pressure is necessary for the alloying of calcium and iron. It was thought that strontium and iron would unite at atmospheric pressure. To test this assumption some iron, reduced by hydrogen (90 per cent.), was put into a hard glass tube, a few pieces of strontium placed on top of it, and the whole covered with iron. The tube was drawn down to a capillary and then sealed off, when the end containing the mixture was heated to low redness. It was then heated in a good blast lamp. When the fusion point of glass was reached the sides of the tube just above the iron fell inward; heat was applied until the glass began to be blown outward. When a bright red heat was reached, portions of the contents were seen to glow. Upon breaking open the tube, a lump of rather hard metallic alloy was found inside. On filing, it presented a bright homogeneous metallic surface; the luster soon disappeared, however. The alloy decomposed water readily. On analysis it gave:

	Per cent.
Insoluble	0.32
Iron	70.14
Strontium	22.95

An alloy was made by fusing iron by hydrogen in the electric furnace and then plunging strontium into the molten mass. A better one, however, was obtained, by plunging the metal into molten cast iron. Each slowly evolved hydrogen from water.

PHILADELPHIA, PA.

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[1] Dissertation, Freidrich Wilhelm Universität, Z. Berlin, 1907

[2] *Proc. Am. Electro-chem. Soc.*, **13**, 143.