the critical solution temperature. Above 45° they diverge again, however, before becoming identical once more at the critical solution temperature, where the two layers become identical. In other words, the water layer has a lower surface tension than the phenol layer up to 45°, where they are identical, and then becomes the larger with an increase in temperature, before they converge again at 68.8°. This behavior is entirely unforeseen by any theory of such systems.

By the aid of the known concentrations and temperatures of this system, through the temperature relationship of the surface tension, a complete survey of this system has become possible, by the use of which one can find the concentrations of the two co-existing layers and their surface tensions at any desired temperature.

IV. Although with the amyl alcohol–water system the surface tensions were studied at a number of temperatures, its high critical solution temperature makes it impossible to prepare a complete survey of this system.

In accord with the results of the other systems, however, it is shown that the values of the surface tension of the two layers always approach very closely that of the non-aqueous component, and have no relations apparently to the value of the other component, water.

V. With the system triethylamine–water great difficulty was experienced in studying the water layer, owing to the fact that the change in concentration with the temperature is very large, and the true equilibrium under the conditions of the experiment very difficult to attain.

Here, again, a complete survey is possible, even though not as accurate as that of the phenol–water system. The most striking thing about the water layer of this system lies in the fact that its surface tension *increases* with increased temperature, due to the loss of triethylamine with the increased temperature.

NEW YORK CITY.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF WISCONSIN.]

THE REDUCTION OF SELENIC ACID.[1]

BY E. B. BENGER.

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Ever since the time of Mitscherlich, who discovered selenic acid, his statement[2] that selenic acid is not decomposed by hydrogen sulfide has stood unquestioned in the literature. Some observations[3] made in this

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[1] Abstract of a part of a thesis submitted to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

[2] *Ann. Phys.*, [1] 9, 629 (1827).

[3] Victor Lenher, private communication, Lenher and Diemer, private communication, H. H. Morris, *Proc. Wis. Acad. Sci. Arts Letters*, 19 (1917).

laboratory during the past few years seemed to indicate that hydrogen sulfide does act upon pure selenic acid. These observations lead to the work described here.

Theoretical Considerations.

If we assume that hydrogen sulfide is able to reduce selenic acid completely to selenium and water we can show that 106,550 calories of heat would be evolved in the reaction. Similarly the reduction by sulfur dioxide, if possible, should be accompanied by the evolution of 114,230 calories of heat. Chemists generally admit that thermochemical data cannot be relied upon to furnish absolute evidence of the possibility of causing a particular reaction to proceed; however, if Berthelot's principle of maximum work is even roughly applicable, a reaction which would be accompanied by the evolution of so large an amount of heat as 100,000 calories would be expected to take place if the proper conditions were obtained.

Krafft and Steiner[1] have shown that sulfur directly displaces the selenium in diphenyl selenide, selenious acid or selenic acid. Thomsen[2] has shown, by the heats of formation of oxidized compounds, that selenium has less affinity for oxygen than either sulfur or tellurium. The small affinity between selenium and oxygen is further illustrated in the reduction of selenic acid by hydrochloric acid[3] and hydrobromic acid[4] and in the ability of selenic acid to dissolve gold by its oxidizing power.[5]

All these facts point to the possibility of reducing selenic acid by hydrogen sulfide and sulfur dioxide.

Materials used.

Selenic Acid.—The method of J. Thomsen[6] as modified by Morris[7] was chosen for the preparation of this compound. The method may be described briefly as follows: Selenium was dissolved in dilute nitric acid, the solution evaporated, the dry residue taken up with water and barium hydroxide solution added as long as a permanent precipitate formed. After filtering, the solution was evaporated to dryness and the resulting selenium dioxide was sublimed until perfectly white. The pure selenium dioxide was dissolved in water and a slight excess of a solution of silver nitrate added, precipitating white, crystalline silver selenite which was filtered and washed thoroughly. The silver selenite was then suspended in water and pure bromine added a little at a time, with vigorous shaking, until a slight excess was present. The precipitated silver bromide was

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[1] *Ber.*, 34, 560 (1901).

[2] "Thermochemische Untersuchungen," II, 279 (1882).

[3] Mitscherlich, *Loc. cit.*

[4] Gooch and Scoville, *Am. J. Sci.*, [3] 1, 402 (1871).

[5] Lenher, THIS JOURNAL, 24, 354 (1902).

[6] *Ber.*, 2, 598 (1869).

[7] *Loc. cit.*

filtered off and the solution concentrated and freed from bromine by heating under reduced pressure. When the acid had been concentrated to about one-half of its original volume it was cooled and treated with hydrogen sulfide gas to remove any selenious acid present. The precipitate of selenium and sulfur was filtered off and the solution returned to the retort and concentrated to the desired extent.

The anhydrous selenic acid used was made by concentrating the acid prepared as above at a very low pressure and a more elevated temperature. Stick potassium hydroxide was placed in the condenser to facilitate the dehydration[1] This acid solidified at —27.5° and thereafter remained solid up to the melting point, 58°.

Hydrogen Sulfide.—This gas was made by the action of hydrochloric acid on sodium sulfide. It was washed with sodium sulfide solution and dried with calcium chloride before use.

Sulfur Dioxide.—The material used was that on the market in liquid form; tests showed it to be sufficiently pure for the present purpose.

Water.—The water used in making selenic acid, preparing all solutions and for final rinsing of vessels was distilled from alkaline permanganate and condensed in a block-tin condenser.

Bromine.—The bromine used in the preparation of the selenic acid was purified from reducing matter by allowing it to stand several days in contact with chromic-sulfuric acid and finally distilling from the mixture.[2]

Experimental.

Reduction by Hydrogen Sulfide.—In a preliminary series of experiments it was shown that 30–70% solutions of selenic acid are decomposed by hydrogen sulfide gas at temperatures from 30° to 90°, and that the amount of the reduction increases with the temperature and concentration of the acid, as well as with the time. The extent of the decomposition was determined by analyzing the solution by various methods or by determining the amount of selenium in the precipitate. No consistent results were obtained, for the reaction is very complicated, as will be shown later.

The following experiments were carried out to determine whether hydrogen sulfide would reduce selenic acid completely:

Fifteen cc. of 10% selenic acid solution were placed in a small bottle immersed in a paraffin bath and dry hydrogen sulfide was passed through the solution. The bath was heated so that in an hour and forty minutes the temperature rose from 55° to 168°. During this time a precipitate of sulfur and selenium appeared and continued to increase, until at the end of the period the contents of the tube were completely changed to a solid, nearly black, mass. The selenic acid had, therefore, been completely de-

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[1] Cameron and Macallan, *Chem. News*, **59**, 232 (1889).

[2] Morris, *Loc. cit.*

composed 112° below the temperature at which selenic acid spontaneously breaks up into selenium dioxide, water and oxygen.[1]

A similar experiment was carried out with the bottle containing the 10% selenic acid immersed in a thermostat set at 95°. The outlet tube from the bottle became plugged with sulfur, thus interrupting the flow of gas, but at the end of 38 hours the selenic acid was completely reduced, only sulfur and black, elementary selenium being left.

With the thermostat kept at 45° complete decomposition of a similar solution took place in thirteen and one-half hours of treatment with hydrogen sulfide.

A 66% solution of selenic acid when chilled to 0° and treated with hydrogen sulfide gas gave an immediate and heavy precipitate of selenium and sulfur. A somewhat smaller precipitate was produced in 40% acid at 0°. Ten per cent. selenic acid at the same temperature gave an immediate and distinct precipitation on treating with hydrogen sulfide. When hydrogen sulfide was bubbled through a 10% solution of selenic acid at —10° a distinct coloration was produced at once.

Krafft and Steiner[2] state that sulfur decomposes selenic acid of nearly 100% concentration only when the temperature is raised above 50°. The experiments carried out at 45°, or at a lower temperature, show that in the reduction of selenic acid by hydrogen sulfide the sulfur freed by oxidation of the hydrogen sulfide plays no part in the further reduction of the acid.

When the reaction was carried out at higher temperatures the odor of sulfur dioxide was always noticed in the bottles in which hydrogen sulfide had reduced selenic acid, and qualitative tests showed the presence of this gas. Sulfur was always deposited on the upper walls of the reaction bottle and the outlet tube was frequently plugged with sulfur. This sulfur was doubtless deposited by the interaction of hydrogen sulfide and sulfur dioxide.

The reduction of selenic acid by hydrogen sulfide may be expressed, in part, thus:

$$H_2S + H_2SeO_4 = 2H_2O + SO_2 + Se$$

The sulfur dioxide and hydrogen sulfide then react, depositing sulfur. The total reaction may be written

$$3H_2S + H_2SeO_4 = 4H_2O + Se + 3S,$$

although it will be shown later that the reaction is not as simple as would appear from these equations.

In view of the facts given it seems that selenic acid of any concentration may be completely decomposed by bubbling dry hydrogen sulfide through the solution. The reaction takes place even at —10°, but progresses more

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[1] Cameron and Macallan, *Loc. cit.*

[2] *Loc. cit.*

rapidly at more elevated temperatures; the reaction is also more rapid in more concentrated solutions.

Reduction by Sulfur Dioxide.—In the first experiment sulfur dioxide was passed through 15 cc. of 10% selenic acid, the temperature being gradually raised from 60° to 130°. A red precipitate appeared during the first minute of treatment and constantly increased. After an hour the volume of the liquid was reduced to about 3 cc. and a black, finely divided precipitate had settled out. When the treatment had extended over six hours the volume of the liquid was about two cc. but there was no other change. The contents of the tube underwent no further change during the next twelve hours of treatment. Thin layers of the mixture showed the characteristic blackish green color of a solution of selenium in sulfuric acid. On dilution with water, a very heavy, thick, red precipitate appeared and much heat was evolved. The filtered liquid gave tests showing the presence of selenic, selenious, sulfurous and sulfuric acids. This experiment indicates that selenic acid is partly decomposed by sulfur dioxide at 130°.

Forty-four hours of treatment of selenic acid with sulfur dioxide at 66° produced similar results.

To determine whether the sulfuric acid, which was formed in the reaction and concentrated by the evaporating action of the dry sulfur dioxide, had stopped the reduction, the following experiment was carried out: The reaction between the selenic acid and sulfur dioxide was made to take place at 130°. When the volume of the solution was reduced to a minimum, as judged from earlier experiments, the mixture was diluted with water and the treatment with sulfur dioxide was resumed. When the solution again became concentrated the dilution and subsequent treatment with the gas were repeated. This procedure resulted in complete reduction of the selenic acid, proving that in the presence of sufficient water selenic acid may be completely reduced by sulfur dioxide.

When sulfur dioxide was allowed to react with selenic acid at temperatures above 130° the residue did not take on the greenish black appearance above referred to, but a mass of fine, white, needle-shaped crystals was found, together with a small volume of a clear and colorless liquid. Qualitative tests indicated that the crystals were selenium dioxide and the results of analyses confirm the tests:

% Se found: (1) 71.12 (2) 71.90. Calc. for SeO_2: 71.12.

It thus appears that the reduction of selenic acid by sulfur dioxide progresses in two steps, which may be represented by the following equations:

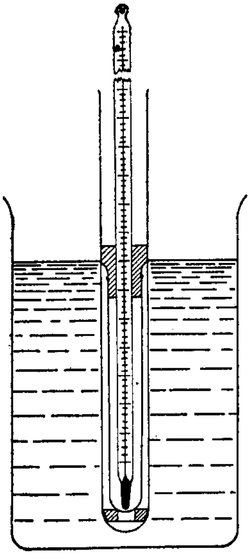
$$H_2SeO_4 + SO_2 = H_2SO_4 + SeO_2,$$

$$2H_2O + SeO_2 + 2SO_2 = 2H_2SO_4 + Se,$$

the total reaction being

$$H_2SeO_4 + 3SO_2 + 2H_2O = 3H_2SO_4 + Se.$$

Reduction by Sulfur.—It is known that sulfur reduces concentrated selenic acid and it seemed important to look into the conditions under which this reduction takes place, since sulfur is liberated in the reaction between selenic acid and hydrogen sulfide. It is conceivable that this reduction might be partly due to the sulfur under some conditions. Cameron and Macallan[1] and Krafft and Steiner[2] have studied the action of sulfur on the crystallized acid. The former investigators found that the action begins at 63°, the latter reported that the action starts at 50° and progresses rapidly at 55°.



Crystals of anhydrous acid were mixed with dry flowers of sulfur, and heated in the apparatus sketched.

The small thin-walled inner tube which contained the mixture was closed with a rubber stopper through which passed a thermometer. This tube was enclosed in a test tube, but kept out of contact with it by a cork at the bottom and the protruding top of the rubber stopper above. The tubes were immersed, as shown, in a beaker of water, the temperature being raised very slowly. No change took place until the temperature reached 58° when the acid melted. At exactly 63° small black spots appeared in the mixture and extended rapidly, with concomitant evolution of sulfur dioxide, until the whole mass was brown or black in color. The experiment was repeated with a fresh mixture and the same results were obtained. Cameron and Macallan's work is thus verified. The failure of Krafft and Steiner to get the true temperature is probably connected with the fact that the melting point of the acid they used was 4° too high.

A similar experiment showed that the reaction between sulfur and 94.2% solution of selenic acid begins at 68°.

Sulfur and 66% selenic acid were sealed in a glass tube and heated to 160° in a paraffin bath. After sixteen hours a few small black spots of selenium appeared under the surface of the selenic acid, and sulfur dioxide was detected upon opening the tube. The reduction had barely started, only a small percentage of the selenic acid present being decomposed.

Forty per cent. acid, when mixed with flowers of sulfur and heated to

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[1] *Chem. News*, 59, 267 (1889).

[2] *Loc. cit.*

190° in a sealed tube, showed no indication of reduction after two hours; but after 16 hours of this treatment the reduction had started.

It thus appears that selenic acid in anhydrous condition is easily reduced by sulfur at 63°; aqueous solutions are reduced at more elevated temperatures. These experiments indicate that when selenic acid oxidizes hydrogen sulfide, under the conditions described in the first part of this paper, the sulfur freed plays no part in the further reduction of the acid.

Reduction by Selenium.—When hydrogen sulfide reduces selenic acid, selenium, as well as sulfur, is liberated. There appears to be no record of experiments to determine the action of selenium upon solutions of selenic acid, and the following work was carried out to ascertain whether the selenium thus liberated has any part in the reduction of the acid.

Thermochemical data show that the reaction should be accompanied by the liberation of 15,160 calories of heat.

The method employed for the investigation was as follows:

Selenic acid of a certain concentration and finely powdered, elementary, metallic selenium were sealed in heavy-walled glass tubes about 1 cm. in diameter and 10 cm. long. Various concentrations of selenic acid, from 1 to 90%, were employed, and in different experiments the temperature was varied. After the treatment had extended over the desired period of time the tubes were opened and the contents washed out and filtered. The dilute solution was then acidified with hydrochloric acid and the undecomposed selenic acid precipitated by excess of barium chloride solution. The filtrate was treated with hydroxylamine hydrochloride, and boiled, which reduced any selenious acid present to red elementary selenium. Very small traces of selenious acid give a distinct coloration by this treatment. A minute amount of barium selenate remains in solution and is reduced to selenium by the action of the hot hydrochloric acid and hydroxylamine hydrochloride. The selenium thus freed produces only a slight pink coloration and was easily distinguished from the intense red color or precipitate caused by reduction of appreciable amounts of selenious acid.

The concentrations of selenic acid employed in the first experiment were 70, 60, 40 and 20%. The samples were sealed, with excess of selenium, in glass tubes and immersed in a paraffin bath heated to 160°. After 30 hours of treatment the selenic acid in each tube was partly decomposed. The amount of reduction increased with concentration of the acid, but in no case was the reaction complete.

In the second series of experiments, 90, 70, 40 and 20% solutions of selenic acid were treated with selenium at 110°. In five hours all of the samples had undergone some reduction, but the reduction was still incomplete after ten days.

The concentrations of selenic acid employed in the third series of experiments were the same as those employed in the second series. The temperature of the bath was 60°. There was some reduction in all of the samples after two days, the amount of change being in the order of the concentration of the acid. At the end of four days the reaction had progressed further, but was still incomplete.

The fourth series of experiments was carried out at room temperature. A 1% solution showed the first indication of decomposition after twelve days; a 20% solution after four days; while 40, 70 and 90% solutions were appreciably reduced in twenty-four hours. The 90% solution was still incompletely decomposed in sixteen days, although the reduction had progressed greatly.

Selenic acid of all concentrations is easily reduced by selenium, the reaction taking place even at room temperatures. At higher temperatures and in more concentrated solutions the reaction is more rapid.

Conclusion.

The reduction of selenic acid by hydrogen sulfide is not a simple process. The first products of the reaction are water, selenium and sulfur; the sulfur is subsequently partly oxidized to sulfur dioxide. Each of these reaction products, except water, possesses the power of independently reducing selenic acid. Furthermore, the reduction by sulfur dioxide occurs in two distinct steps, and it is highly probable that the reaction brought about by hydrogen sulfide is similar in that respect. Thus the reduction of selenic acid by hydrogen sulfide involves from six to eight separate reactions. The heterogeneity of the system adds to the complications. In this system selenium and sulfur exist as solids; in the liquid phase are selenic acid, selenious acid, sulfurous acid, sulfuric acid, hydrogen sulfide and water; in the gas phase are hydrogen sulfide and sulfur dioxide.

Considering the complexity of the reaction it is not surprising that attempts to accurately measure the rate of the reduction of selenic acid by hydrogen sulfide should have met with failure.

Summary.

1. The often-occurring statement that selenic acid is not decomposed by hydrogen sulfide is erroneous. Selenic acid of any concentration may be completely decomposed by dry hydrogen sulfide gas at any temperature above —10°. The rate of reduction increases with both the temperature and the concentration of the acid. Selenic acid in 10% solution, at 45°, may be completely decomposed by dry hydrogen sulfide gas in thirteen and one-half hours.

2. Sulfur dioxide reduces selenic acid. The reaction takes place in two steps and selenium dioxide has been separated as an intermediate product. When the sulfuric acid reaches a certain concentration the reducing action

stops, but when the solution is diluted the reaction can proceed to completion.

3. Sulfur reduces anhydrous selenic acid at 63°. In aqueous solution the reaction takes place at higher temperatures, thus a 94.2% solution of the acid is attacked at 68°, and a 40% solution at 190°.

4. Selenium reduces selenic acid of all concentrations at room temperature, or more rapidly at more elevated temperature. More concentrated solutions are more readily attacked.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF WISCONSIN.]

ON THE REDUCTION OF TELLURIC ACID.[1]

BY E. B. BENGER.

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The study of selenic acid, presented in the preceding paper, has brought new light on the oxidizing power of that compound. Selenic acid is much more easily reduced than was known hitherto. It seemed of interest to determine whether telluric acid would be reduced by substances which reduce selenic acid.

Tellurium lies in the same group and family as selenium, having the highest atomic weight of the members of the sulfur family.

Sulfuric acid is capable of exerting oxidizing power only when in concentrated solution and at elevated temperatures. Selenic acid, as has been shown, is an oxidizing agent toward hydrogen sulfide and sulfur dioxide at all temperatures and even in dilute solutions. Telluric acid, being analogous to sulfuric and selenic acids, and of higher molecular weight, might be expected to show still greater development of the oxidizing power. However, telluric acid differs, in some important respects, from these similar compounds. It is a solid, whereas both of the others are liquids at the ordinary temperature, it has no such strong affinity for water as that shown by either sulfuric or selenic acids, and it is a much weaker acid, being about as strong as hydrogen sulfide or hydrocyanic acid.[2] In these respects it is quite distinct from the lower members of the group. Tellurium itself, in its atomic weight, is an important exception to the rules underlying the periodic system.

Materials Used.

Telluric Acid.—The telluric acid used was prepared by the method of Staudenmaier.[3] This method, which has been employed in this labora-

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[1] Abstract of a part of a thesis submitted to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

[2] Gutbier, "Studien über das Tellur," Leipzig, 1912.

[3] *Z. anorg. allgem. Chem.*, 10, 189 (1895).