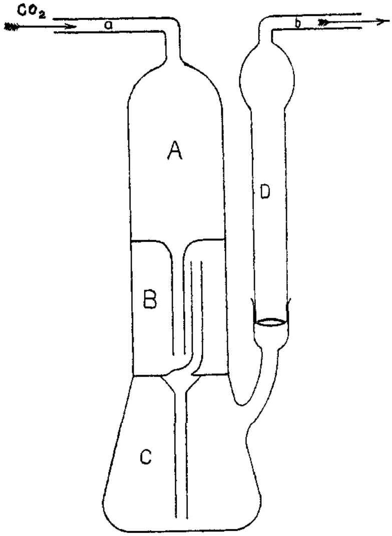

partments *B* and *C* contain as much of the solution as would completely fill *A*, which is about thirty-five to forty grams of a 2 : 3 solution. *D*, which is fastened to the bulb by means of a ground-glass joint, contains solid potassium hydroxide, or soda-lime, supported by a plug of glass-wool. The liquids in *B* and *C* can be easily mixed when desired, by applying suction at *a*. The bulb, when filled and ready for use, weighs from sixty-five to seventy grams, and undoubtedly can be made even much lighter.

The total number of compartments is thus reduced from five in Geissler's form to three in the form here presented, while the absorbing chambers are reduced only from three to two. The construction of the bulb is such that *C* can never get overfilled by the solution from *B*.

This form of a potash bulb possesses the advantages first, that it can be easily handled and wiped, presenting the outside surface of an ordinary small flask, and second, that it can be set without any support, and can be weighed without suspending it if so desired.

I wish to express my thanks to the firm of Greiner & Friedrichs, of Thüringen, who have kindly made the bulb for me in a most satisfactory manner.

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REDUCTION OF CONCENTRATED SULPHURIC ACID BY COPPER.

BY CHARLES BASKERVILLE.

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IN a previous communication[1] the writer noted that copper was acted upon by concentrated sulphuric acid (1.84 sp. gr.) not

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[1] This Journal, 17, 90.

only at the ordinary temperatures of the air, 20°–30° C., but at zero as well. Andrews[1] states that the assertion is incorrect and that it does not occur until the temperature 86° C. has been reached, or a point above the dissociation temperature of the concentrated sulphuric acid, 67° C., according to him. Andrews further says that the author's statements were based "not upon any demonstrations of the formation of sulphurous acid, but solely on the formation of copper sulphate," which, he says, occurs only "in consequence of the presence of the air." It is to be regretted that Dr. Andrews did not note carefully the statements of the author in his previous communication, as no reason whatever exists for any such conclusions, because it was distinctly stated that not only the copper as sulphate, but as sulphide was determined, as well as sulphurous acid, and moreover, that the experiments were carried out when the air had been replaced by a neutral gas, either hydrogen or carbon dioxide.

The author, although confident of the correctness of his former statement, carried out further experiments to correct the error, if committed or to establish, beyond question, the fact that concentrated sulphuric acid of 1.84 sp. gr. is reduced by copper below 86° C., the limit *positively* set by Dr. Andrews.

The fact that these experiments but confirmed the former statement of the author allows the incorporation of the results in this paper.

As far back as 1834 the fact that copper is acted upon by concentrated sulphuric acid at ordinary temperatures, if sufficient time be given, was made known by Barruel.[2] Calvert and Johnson,[3] however, failed to obtain any action below 130° C. and considered that none took place. Pickering,[4] however, stated that "sulphuric acid attacks copper at all temperatures from 19° C., (and probably even still lower) upwards."

First Experiment.—Copper ribbon in strips, 1 x 3–4 cm., was submerged in concentrated sulphuric acid in a clean glass stoppered flask for a month. At the end of that time not only were there white crystals of anhydrous copper sulphate clinging to

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[1] This Journal, 18, 253.

[2] *J. de pharm.*, 20, 13, *1834*.

[3] *J. Chem. Soc.*, 19, 438, *1866*.

[4] *J. Chem. Soc.*, Trans., *1878*, 113.

the sides of the containing vessel, but there was a very appreciable amount of brownish black cuprous sulphide and sulphur dioxide was easily detected by its strong odor when the vessel was opened.

Andrews[1] states "that in the presence of air sulphuric acid is attacked by copper at ordinary temperatures, but without reduction of the acid. The reaction must take place according to the equation,

$$2Cu + O_2 + 2H_2SO_4 = 2CuSO_4 + 2H_2O."$$

Formerly the author[2] stated that the presence of the oxygen of the air when it comes into contact with the copper in the acid has great influence on the reaction. Fifty years ago, Maumené[3] proved that when a current of oxygen gas was passed through the boiling acid, the amount of insoluble residue, *e. g.*, cuprous sulphide, was diminished, that is, less than there would be formed if the experiment were carried out with a current of carbon dioxide. The copper must be directly exposed to the oxygen by only partial submersion or the bubbling of the air against or around the submerged copper; but the air in a confined space, not at all in contact with the copper, but separated by a thick layer of concentrated sulphuric acid, has little or no effect.

Yet grant that the oxygen of the air (volume of air about 200 cc.) confined in the flask, had been utilized in the formation of the copper sulphate produced. According to the formula given above, the oxygen would be absorbed and no corresponding amount of any other gas would be eliminated; consequently there should be a greater external pressure at the close than at the beginning of the experiment. When the smoothly fitting glass stopper was removed, not only no extra internal pressure was noticed, but in fact a pressure from within. This was evidently produced by the sulphur dioxide generated. The sulphur dioxide was swept out by a current of air through a dilute solution of potassium permanganate, which was quickly bleached. The presence of sulphur dioxide was further proven by the addition of barium chloride to the bleached potassium permanganate

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[1] This Journal, **18**, 252.

[2] *Ibid*, 17, 912.

[3] *Ann. chim. phys.*, *1846*, [3], **18**, 311.

solution. Nor does the formula given above account for the cuprous sulphide which is always produced.

Second Experiment.—Realizing the possibility of some organic matter or dust remaining in the flask, although it had been carefully cleansed, the first experiment was repeated with the greatest precaution to ensure the absence of dust. The flask was scoured with boiling concentrated pure sulphuric acid containing potassium bichromate and carefully cleansed with distilled water. The last traces of water were removed by four subsequent washings with the same kind of concentrated acid used throughout the experiments. The experiment was carried out in the same manner as the first, the same results being obtained.

A blank experiment was carried out at the same time. The flask was rendered dust free in the manner just mentioned and fifty cc. of the same acid allowed to remain in the flask for six months. At the end of that period not a trace of sulphur dioxide could be detected in the blank, therefore the sulphur dioxide produced when the copper was inserted could not be due to the reduction of the sulphuric acid by an extraneous substance, but solely by the copper. The conclusion is that sulphuric acid is reduced by copper when air is present at the ordinary temperatures, 20°–30° C.

Third Experiment.—An ordinary Kjeldahl digestion flask was made dust free by the treatment noted above. 100 cc. sulphuric acid, 1.84 sp. gr., were placed therein and clean dry strips of copper ribbon were completely submerged in the acid. Now air-free carbon dioxide was passed through the flask for three hours. The inlet tube was just dipped into the acid. The flask was then attached to a suction pump, with a sulphuric acid drying flask intervening to prevent a possible return flow of gas or air which might carry moisture or dust into the flask. The flask was exhausted of the carbon dioxide present for three hours at a pressure of 150 mm. It was then sealed with the blast lamp and placed aside in a darkened cupboard. Observations were made every few days to note any reaction taking place. Within two days it could be easily seen that copper sulphate had been formed and the liquid was somewhat clouded by very finely divided suspended cuprous sulphide. Continued observations extending over a period of seven weeks showed only an increase in the amounts of both of these substances. The temperature of the cupboard had at no time risen above 20° C., and was for most of the time much lower. The flask was then opened as any other sealed tube, and instead of an external pressure inward, which had been sufficient to heavily dent the tube in sealing, there was a strong internal pressure outward. The gas evolved was sulphur dioxide, easily detected by its strong odor and bleaching effect upon a dilute solution of potassium permanganate. The sulphuric acid produced by the oxidation of the sulphur dioxide by the permanganate was precipitated by barium chloride. All solutions and apparatus were proven to be free from traces of sulphur dioxide and sulphuric acid by a blank experiment.

Conclusion.—Concentrated sulphuric acid, 1.84 sp. gr., is reduced by copper when air is absent and at temperatures far below 86° C., in fact at the ordinary atmospheric temperatures with the formation of copper sulphate and cuprous sulphide and the production of sulphur dioxide.

Finally.—Apparatus similar to that made use of by Andrews[1] was employed with the modification of having three drying flasks containing concentrated sulphuric acid instead of one, and a Meyer absorption tube was substituted for a single small flask. These served merely as extra precautions against dust and insured an intimate mixing of the outgoing gases with the permanganate. Within twelve hours the permanganate was bleached. Andrews' experiment lasted only fifteen minutes. The presence of the sulphur dioxide produced was easily detected by the odor when the apparatus was opened, and in the bleached permanganate solution by barium chloride. Copper sulphate and cuprous sulphide were also formed.

Concentrated Sulphuric Acid is Acted upon by Copper at Zero.—Quantitative experiments were carried out by the author when the concentrated sulphuric acid in which the copper was submerged was practically at zero.[2] In stating the results, however, the author gave the temperature as "0°–10° C." The flask

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[1] This Journal, 18, 251.

[2] *Ibid*, 17, 908.

containing the acid was buried in an ice-bath and the temperature of the liquid noted by a thermometer inserted through a rubber stopper. The apparatus was air-tight. A stream of hydrogen gas was continued through the apparatus in one experiment for six weeks and in another two months. On two occasions when the ice in the bath had melted in going over Sunday, the temperature rose to 10° C. The temperature could not possibly have remained that high for over twelve hours, which would have had small influence when the experiments lasted through a number of days. The temperature was reported 0°–10° C., however. Not only copper sulphate, but cuprous sulphide and sulphur dioxide had also formed. Copper, therefore, decomposes concentrated sulphuric acid (sp. gr. 1.84) practically at zero.

From my own experiments and from experiments performed with apparatus similar to that used by Andrews and under the same conditions, except with regard to the important element, time, which consideration is necessary for all chemical reactions, the author must adhere to his former statement.

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THE SEPARATION OF THORIUM FROM THE OTHER RARE EARTHS BY MEANS OF POTASSIUM TRINITRIDE.

BY L. M. DENNIS.

Received September 4, 1896.

SOME time ago the author and F. L. Kortright[1] briefly described the action of a solution of potassium trinitride upon a neutral solution of the rare earths. It was found at that time that the flocculent precipitate which is produced was most probably thorium hydroxide, but our supply of potassium trinitride having been exhausted it was impossible to further investigate the reaction or ascertain the completeness of the separation. The immediate continuation of the work was prevented by unexpected difficulties which were encountered in the preparation of pure hydronitric acid on a large scale. These difficulties have since been removed, and it has been possible to prepare an amount of the reagent sufficient for the investigation described below.

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[1] *Ztschr. anorg. Chem.*, 6, 35; *Am. Chem. J.*, 16, 79.