

nisse." In reply to this we offer the following experiments:

Experiment 1.—To a solution containing 0.3893 gram of copper sulphate (= 0.0988 gram of copper) and 0.1152 gram of cadmium oxide (= 0.0985 gram of cadmium) were added two cc. of nitric acid, sp. gr. 1.43. The total dilution of the solution equaled 100 cc. It was heated to 50° C., and electrolyzed with a current $N.D._{100} = 0.10$ ampere. Voltage 2.5. The metal was completely precipitated in three hours. It was bright in color and satisfactory in every respect. It weighed 0.0988 gram and did not contain cadmium.

Experiment 2.—A solution containing the same quantity of copper and 0.1203 gram of cadmium oxide, when treated exactly as in Experiment 1, gave 0.0987 gram of copper. It was free from cadmium.

To these results we would add the observation of Neumann:¹ "Am einfachsten is zur trennung von Kupfer und Kadmium immer die Verbindung der mit *freier Salpetersäure* versetzten Lösung beider Salze."

Heidenreich maintains that the separation of copper from cadmium succeeds "sicherer aus einer mit *Schwefelsäure* versetzten Lösung." This solution had been previously recommended by Smith,² and his observations were confirmed by Freudenberg.³

The results recorded in the preceding paragraphs justify us in saying that cadmium can be successfully determined electrolytically when working either with its acetate or sulphate, and that its separation from copper in the presence of nitric acid is in every respect satisfactory.

The failure of Heidenreich to precipitate uranic oxide by means of the current will be considered later.

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ON THE REACTIONS BETWEEN MERCURY AND CONCENTRATED SULPHURIC ACID.

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MANY text-books class the reactions between copper and concentrated sulphuric acid along with mercury and sul-

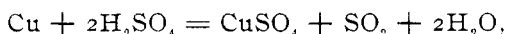
¹ Elektrolyse. p. 169.

² See Electrochemical Analysis, 2nd. Ed., p. 108.

³ Ztschr. phys. Chem., 12, 97.

phuric acid, stating merely that a sulphate of copper or mercury is formed with the evolution of sulphur dioxide.

In other communications¹ one of us, (Baskerville) has shown that while the formula

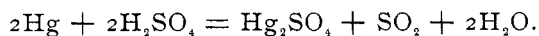


expresses in fact the main reaction when these two substances are brought together, even at different temperatures, that only at 270° C., or higher, is that reaction unaccompanied with very important and complex secondary reactions. In preparing sulphur dioxide, by heating together copper and concentrated sulphuric acid, invariably a black or brown material discolors the colorless acid. This dark substance is, in the main, cuprous sulphide.

Not finding the reaction between mercury and concentrated sulphuric acid worked out in detail in any of the literature at our command and since so much wrong data have been recorded concerning copper under similar conditions, it was deemed advisable to study this reaction at different temperatures.

The reaction is by no means like that of copper. The primary reaction depends upon the preponderance of mercury or acid, the temperature, and the time during which it is allowed to continue.

If the mercury be in larger amounts than the acid, invariably almost pure mercurous sulphate is produced :



It will be well to state here that the mercurous sulphate so produced is a white crystalline substance and not black, as stated in Roscoe and Schorlemmer's Treatise on Chemistry.²

Series of experiments in duplicate were carried out at different temperatures when the acid was in large excess. A qualitative experiment showed that mercury decomposed concentrated sulphuric acid at the ordinary atmospheric temperature, about 20° C. This experience is contrary to that stated in a number of text-books. Experiments carried out at 100° C. upon a water-bath, lasting during twenty hours, in apparatus especially arranged to insure only the presence of dust-free, dry air

¹ This Journal. 17, 904, and 18, 942.

² Vol. II, Part I, p. 401.

showed that about one-fifth of the mercury had entered into the reaction. Ten grams of the mercury and from fifty to 100 grams acid were used. Expecting the results to exhibit this reaction,



we were surprised to find so much less sulphur dioxide evolved than should have been. The crystalline sulphate produced gave 20.75 per cent. SO_2 , which is very near 19.35 calculated for mercurous sulphate. Again, at 150°C ., when the flask containing the mercury and acid was kept at a practically constant temperature by being immersed in a sulphuric acid bath for two hours, the amount of sulphur dioxide evolved was much below the theoretical. At least half of the mercury in each of these experiments was dissolved. The white crystalline layer of sulphate which separated out as the amount of metallic mercury decreased was augmented by another layer, which had been in solution, when the acid became cool. Both were crystalline, but while the latter was powdery the former was composed of needle-like crystals. To avoid the formation of the basic sulphate, $\text{HgSO}_4 \cdot 2\text{HgO}$, which was always produced in our efforts to wash out the remaining acid with water, we used ninety-five per cent. alcohol. Four washings were sufficient; in fact, on further washing even with alcohol some basic sulphate was formed. On analysis of this alcohol-washed substance, which had been dried to a constant weight at 100°C ., we obtained:

	Calculated for $\text{Hg}_2(\text{SO}_4)_2$, or $\text{Hg}_2\text{SO}_4 \cdot \text{HgSO}_4$.	Found.
SO_2	24.24	23.96 24.27
Mercury (-ous).....	50.38	50.27

At 200°C . the percentage of mercurous mercury dropped to 40; at 250°C . still lower, showing a steady decrease in the amount of mercurous sulphate produced as the temperature increased. When the acid was boiled and the mercury poured in, the crystalline compound gave 32.91 per cent. of sulphur tetroxide when mercuric sulphate contains 32.43 per cent. Evidently some of the acid was not removed by the washing with alcohol.

It was desirable to determine whether the primary reaction took place in steps, *e. g.*, if the metal liberated hydrogen, which

in the nascent state attacked the remaining sulphuric acid with the production of sulphur dioxide, such having been recorded by some authors to be the case in the reaction between copper and sulphuric acid. Careful experiments at different temperatures, 150° and 200° C., were carried out in an atmosphere of carbon dioxide free from air. One hundred cc. of the gases given off and collected over a ten per cent. solution of sodium hydroxide gave not a trace of hydrogen. The sulphuric acid in this case is evidently reduced directly by the metal. No sulphide was produced, nor any free sulphur.

If portions of the crystalline compound, produced by the treatment of mercury with concentrated sulphuric acid rendered free of acid by washing with alcohol and dried at 100° C., be again treated with acid in similar apparatus, sulphur dioxide is evolved in proportion to the amount of mercurous sulphate there is present. If mercuric sulphate be treated with the acid no sulphur dioxide is evolved. In fact, if a prepared mixture of mercurous and mercuric sulphates in varying proportions, or any of the crystalline compounds obtained in any of the experiments cited, except that produced by the boiling acid, be treated with fresh acid and heated until the gas evolved ceases to bleach a weak potassium permanganate solution, the crystalline residue then obtained is mercuric sulphate.

Although the relative yield of sulphur dioxide is less, the treatment of mercury with concentrated sulphuric acid has been recommended for classroom experiment on account of neatness and freedom from black residue, which in the case of copper is oftentimes unintelligible to the ordinary student. A slight objection may be urged against this use on account of the volatility of the metallic mercury at the temperature of reaction. Faraday has shown that in spite of its high boiling-point, mercury volatilizes at the ordinary temperatures. One of us (Baskerville) has had this fact to contend with in several cases where this method of evolving sulphur dioxide was made use of in quantitative work.

In the experiments given all materials used were pure. The concentrated sulphuric acid was of 1.84 sp. gr. The mercury was purified according to Lothar Meyer's method¹ by allowing

¹ *Ztschr. anal. Chem.*, 2, 241.

the distilled metal to flow in a thin stream first through a column of dilute nitric acid, then dilute sulphuric, to dissolve out all lead and tin, finally washed and dried. All apparatus was most carefully cleansed, and when necessary moisture-free and proved to be air-tight.

UNIVERSITY OF NORTH CAROLINA,
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ON THE DETERMINATION OF FAT AND CASEIN IN FECES.

BY HERMAN POOLE.

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HAVING been called upon to make some examinations of feces from children in connection with the clinical experiments on the Prof. Gaertner mother-milk now being carried on with satisfactory results at the German Polyclinic on Seventh Street, New York City, I began by looking up what had been done on the subject previously. To my surprise I found nothing at all which would give even a fairly approximate idea of the percentage of fat and casein. After consulting all the authorities I could find, I saw that I must work out a new or a fuller method than any previously used.

The problem to solve was this: A certain child takes per day a definite quantity of milk of known composition. It digests a portion of this and passes off the balance undigested. This milk contains fat and casein. How much fat and how much casein pass through undigested, and from this how much of the milk is assimilated?

Of course, one of the first books suggested to an American would be Flint's Physiology, since Flint has done considerable work on this kind of material several years ago. An examination of his work, however, showed that the methods he used and the special objects he had in view were entirely unsuited and foreign to the work I intended. He operated on the feces of adults, and more particularly to discover and extract the unknown and undescribed constituents rather than to actually make accurate determinations of the common and known ones. Besides, the chemical methods in use in his day are to a considerable extent supplanted by more accurate and modern methods.