It is thus possible from purely theoretical knowledge, and a few appropriate simple experiments to find just what solutions must be used for baths for the deposition of any alloy. The contrast between this method and the old empirical one of trying all combinations until a lucky hit is made, the true reasons for which are unknown, is striking, but it is just what is being experienced to-day in all branches of chemistry by the application of theory to practice. The other ingredients which are used in the baths are to produce a fine smooth coating and have nothing to do with the theory of the method. Of course there are other solutions which behave just as the double cyanides do, but as the theory is the same, the only idea of a change would be for economy and that is a question for the technical side of the subject. Such another solution which is used is made by dissolving zinc and copper salts in an excess of ammonia. Here we have just as before Zn and Cu ions, and also complex ones which behave just as $\overset{-}{C}\overset{-}{u}CN_4$ and $\overset{-}{Z}\overset{-}{n}CN_4$.

Another liquid which causes copper to act as a metal of high electrolytic solution pressure is a solution of potassium sulphide.

THE DETERMINATION OF SULPHUR IN BITUMENS.

BY A. C. LANGMUIR.

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IN the September number of this Journal, S. F. and H. E. Peckham criticize a paper by E. H. Hodgson which appeared in November, 1898, and describe, in some detail, their own method slightly modified.

The authors claim for their method that it is "simple, reasonably rapid and accurate" and state that it is "susceptible of great accuracy, if *conducted with care.* It requires great care from the beginning to the end. Mr. Hodgson's results do not indicate great care,—they are not sufficiently concordant."

It is but fair to Mr. Hodgson to call attention to certain features in Messrs. Peckham's method which cannot inspire chemists with confidence and which may possibly indicate that the authors themselves have not bestowed on their method the great care which they miss in Mr. Hodgson's work.

A brief review of the method is necessary: Approximately

0.5 gram of the bitumen is fused with 30 grams of a mixture of equal parts of sodium carbonate and potassium nitrate in a platinum crucible. The crucible contents are dissolved in water, hydrochloric acid is added, and the silica is separated by evaporation on the water-bath and dehydration. After taking up with hydrochloric acid and water the silica is filtered and the filtrate is rendered alkaline with ammonia to precipitate iron and alumina. The excess of ammonia is removed by boiling, and the iron and aluminum are filtered off. The lime is removed by ammonium oxalate and in the filtrate from the latter, now free from silica, alumina, iron and lime, the sulphuric acid is precipitated by the usual method. The convenience of estimating the mineral constituents in the same solution with the sulphuric acid is noted. In our opinion, what is gained in convenience, if any, by this method, is lost in accuracy.

In some bitumens the amount of sulphur is very low. In others the proportion of mineral matter is so high that very considerable amounts of iron, alumina, or lime may be met in the course of the analysis.

If the above method is to be generally applied the following objections should first be answered:

In the course of the fusion with alkaline carbonate and nitrate there is danger of the absorption of sulphuric acid produced by the burning gas. Any error from this cause would be especially noticed in the analysis of bitumens low in sulphur. An alcohol lamp should be used or the crucible should rest in a hole cut in asbestos board to protect the fusion from the access of the products of combustion.

Messrs. Peckham have not given us details sufficient to enable us to decide whether they have made use of these necessary precautions. Several chemists have called attention to this danger.[1]

In the slow evaporation of the fusion on the water-bath there is again a possible source of error in the absorption of sulphur, if, as is often the case, the bath is heated by gas.

Hillebrand[2] finds that the sulphur introduced in this way in the analysis of silicate rocks is frequently as much as the entire sulphur present. The writer's own experience has confirmed

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[1] Price: *J. Chem. Soc.*, London, 2, 51; Fresenius: *Ztschr. anal. Chem.*, 16, 339; Lunge: *J. prakt. Chem.*, 40, 239

[2] Bull. U. S. Geol. Survey, 148, 1897.

this statement entirely and rather than dehydrate for silica we have precipitated the sulphuric acid directly in the acidulated aqueous solution of the fusion. We have never found any silica in the barium sulphate so obtained, but if its presence is feared it may be readily removed with a little hydrofluoric and sulphuric acids.

How considerable the contamination of the evaporating solution may be is plain from the experiment of E. von Meyer[1] who found, after evaporating 2 liters of distilled water down to 50 cc. during six hours on the water-bath, the equivalent of 0.0426 gram barium sulphate present.

A third objection and the most serious of all is against the separation of iron and alumina by boiling out the excess of ammonia. It is well known that iron can only be precipitated free from sulphur in a solution containing the latter by adding a distinct excess of ammonia to the moderately warm solution, heating a few minutes on the water-bath and filtering immediately. Only in this way can the formation of insoluble basic sulphates be prevented. Boiling the solution is, of all things, to be avoided. Lunge[2] states that correct results can only be obtained by adhering strictly to this procedure and that deviations lead to serious errors.

The check analyses made by the authors do not controvert the criticisms just made as the asphalt analyzed was said to be very pure and was presumably free from mineral matter.

Finally, in view of the recognized tendency of barium sulphate to drag down with it other mineral constituents of the solution and barium salts of other acids present, what must be said of precipitating sulphuric acid in the presence of ammonium oxalate and the alkaline chlorides from 30 grams of mixed carbonate and nitrate?

Our preference is given to Eschka's method following the details as described by Heath.[3] The Eschka method is admittedly the best for the determination of sulphur in bituminous coals. The problem here is a very similar one. In addition to its convenience and rapidity the Eschka method has the

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[1] *J. prakt. Chem.*, **42**, 267; see also Gunning: *Ztschr. anal. Chem.*, **7**, 480; Alex: *Ibid.*, **10**, 246; Wagner: *Ibid.*, **20**, 323; Lieben: *Ibid.*, **32**, 214; Privozink: *Ber. d. chem. Ges.*, **25**, 2200.

[2] *Chem. News*, **71**, 132; *J. prakt. Chem.*, **40**, 239.

[3] This Journal, **20**, 630.

advantage of leaving the iron, lime, and alumina insoluble at the start and only a small quantity of alkali is introduced into the analysis.

As for the mineral constituents they are better determined on a separate portion. Their accurate determination is made all the more difficult by the presence of an excessive amount of alkali metals as in Peckham's method.

Our practice has been to heat the asphalt at a low temperature in a platinum dish, slowly driving off the volatile constituents in such a way that the asphalt does not burn. At the end the temperature may be raised and the remaining organic matter burned without danger of loss.

The ash is extracted with hydrochloric acid and any insoluble residue fused with a small amount of the mixed carbonates. The solution of the fusion in hydrochloric acid is added to the other and the analysis proceeded with as usual. In this way the quantity of alkaline salts is reduced to a minimum.

Time is actually lost by determining the metals and sulphur in one portion as the determination of the latter must wait until the metals have been separated.

In all but two of the asphalt analyses of Dr. Day, as quoted by Messrs. Peckham, the decimal point is misplaced, making the per cent. sulphur far less than it should be.

LABORATORY OF RICKETTS AND BANKS, NEW YORK.

THE DETERMINATION OF NICKEL IN NICKEL ORES.

BY A. C. LANGMUIR.

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GEORGE WILLIAM SARGENT'S paper on the "Determination of Nickel in Nickel-Steel" in the October number of this Journal, prompts me to publish a somewhat similar method for the determination of nickel in its ores, which has been in use in this laboratory for several months with excellent results. It is particularly advantageous in all cases in which a relatively small quantity of nickel is to be separated from a large amount of iron and surpasses all other methods such as the basic acetate, basic carbonate, or ammonia separations.

One gram of the ore is covered in a No. 2 Griffin's beaker