

The curves are quite different in trend. Oxalic and citric acids diminish in surface-tension as the concentration increases; the limited solubility of oxalic acid does not permit of an extended comparison of the two acids, however. A curious fact about the curve for citric acid is its being rectilinear and parallel to the x -axis at concentrations varying between thirty-five and sixty-five per cent.; within this range the surface-tensions of the solutions are independent of their concentrations.

The curve for tartaric acid gradually rises, becoming steeper and steeper as the concentration increases. For moderate concentrations it is approximately straight, which, for that matter, is the case with the other two acids also.

The reasons for the peculiarities of these curves are probably to be sought in the possible molecular polymerization and undoubted electrolytic dissociation of the acids in aqueous solution; very complicated relationships are presented, which in the absence of other physical data on the subject, it would now be unprofitable to attempt to unravel.

SODIUM PEROXIDE IN QUANTITATIVE ANALYSIS.¹

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W. HEMPEL² and J. Clark³ first proposed to use sodium peroxide in quantitative analysis. Hempel employed it for the oxidation of chromium, manganese, tungsten, and tin, and subsequent determination by known means; he also mentions that sulphur is completely oxidized to trioxide. He further recommends the reagent for the decomposition of zinc-blende and galena.

J. Clark recommends it for the estimation of sulphur, arsenic, and chromium, also for the separation of manganese from zinc, nickel, and cobalt. He states⁴ that the action of sodium peroxide on coke and coal is too violent for analytical purposes. T. Spüller and S. Kalman⁵ use it on ferrochrome, chrome steel,

¹ A review of various propositions made since 1892.

² *Ztschr. anorg. Chem.*, 1892, 3, 193-194.

³ *J. Chem. Soc.*, 1893, 1079.

⁴ *Ibid.*, 63, 1079.

⁵ *Chem. Ztg.*, 17, 18.

chrome iron, and also sulphurets. Poleck¹ experimented on organic substances, as did J. Tafel.²

In 1894, M. Hoehnel and C. Glaser³ made revised recommendations for the estimation of sulphur in pyrites. O. Kassner⁴ states that iron is precipitated as hydroxide, but not changed into ferric acid, that, on the contrary, solutions of ferric acid are reduced by sodium peroxide. He gives detailed statements concerning separation of chromium and manganese; of the decomposition of freshly precipitated sulphides of antimony, tin, and arsenic. In 1895, L. Archbutt⁵ reports an analysis of sodium peroxide, showing the presence of nearly one-half of one per cent. of iron and alumina in the commercial article. Alb. Edinger⁶ gives his experience in the determination of sulphur and chlorine in inorganic and organic combinations. M. C. Schuyler⁷ proposed to determine mercury in mercuric salts by reduction to metal with sodium peroxide. In 1897 S. W. Parr⁸ reports on the adaptability of sodium peroxide as a third group reagent in qualitative analysis, practically a review of the above-named publications, omitting quantitative features.

The *Chemiker Zeitung*⁹ contains a second note of the author, suggesting some improvements in the determination of sulphur in pyrites and later the same author¹⁰ separated iron from aluminum in phosphates and other minerals by means of sodium peroxide.

It may be in place here to state that the C. P. sodium peroxide of the trade has, as far as I have had occasion to test it, proved quite free from oxide of iron and alumina. It appears therefore probable that the article analyzed by Archbutt was a crude commercial product.

I cannot confirm O. Kassner's statement, that iron is not oxidized to ferric acid by sodium peroxide. If the reagent is added to a solution of an iron salt, without the precaution of

¹ *Chem. Ztg.*, 18, 103.

² *Ber. d. chem. Ges.*, 27, 816.

³ *Arch. Pharm.*, 232, 222; *Chem. Ztg.*, 18, 1448.

⁴ *Arch. Pharm.*, 232, 226.

⁵ *Analyst*, 20.

⁶ *Ztschr. anal. Chem.*, 34, 362.

⁷ *Chem. Ztg.*, 20, 1896.

⁸ *This Journal*, 19, 341.

⁹ *Chem. Ztg.*, 21, No. 6.

¹⁰ *Ibid.*, 21, No. 69.

keeping the temperature of the latter sufficiently low, his statement holds good. But if this last condition is complied with by keeping the solution comparatively cool, a sufficient excess of the reagent will produce a perfect solution, as I have stated in the above, last-named paper.

I desire especially to recur to J. Clark's statement that the action of sodium peroxide on coke and coal is too violent to permit of use in analysis. I have used this reagent in a considerable number of coke, coal, and asphalt analyses for sulphur with perfect success, and I now present a short description of the method as I carry it out.

The material to be analyzed is placed in a sufficiently large silver or nickel dish and covered with about four times its weight of sodium carbonate. Upon this a piece of sodium hydroxide is laid, about one half the weight of the carbonate used.

The dish is now moved carefully and slowly over a small flame until the gas generation subsides and a half-fused mass is obtained. Upon this mass dry sodium peroxide is now dusted from a porcelain or platinum spoon in small quantities at a time, always waiting until the reaction is over. This is continued until all carbon is burned away, when the mass, if necessary, is heated to perfect fusion. Usually this is obtained by the heat generated by the combustion in the dish, which, however, takes place so quietly, that no loss by explosion or spurting will occur. After this operation the determination of sulphur is carried to an end in the well-known way.

I believe that this method will prove quite a relief to those chemists, who have to make many sulphur determinations in coke and coal, and who know the uncertain working of a fusion with potassium nitrate. At least it has been my experience that it is difficult to so regulate the temperature of the fusion as to avoid explosion with loss. Even the use of double crucibles has not always proved successful. The time required for the operation with sodium peroxide is quite short; with coke about five minutes, with coal probably ten, while with asphalt, owing to the peculiar nature of the material, it will take a little longer.

In analysis of chrome ores sodium peroxide does not appear to fulfil the hopes of those chemists who first proposed it. The oxidation is reported to be never perfect in one operation, which

makes the method more complicated and troublesome than a fusion with potassium nitrate and borax.

This was to be expected, since even chromic salts in solution require more than one treatment with sodium peroxide before complete oxidation to chromic acid is effected.

With this exception sodium peroxide has proved a very useful and convenient reagent, applicable in a great number and variety of cases. It ought to be, and no doubt will become, one of the standard reagents of a modern laboratory.

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ADDITIONAL NOTES ON THE SUGAR-CANE AMID.

By EDMUND C. SHOREY.

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IN a paper on the principal amid of sugar-cane, which appeared in this Journal, November, 1897, I gave the result of work done during the last grinding season on the amid present in sugar-cane. Since then I have been able to correct some errors in the work done then, and have also obtained additional proof of the correctness of the conclusion reached that this amid is amidoacetic acid and not asparagin.

The chief error in my former work which I wish to correct now, was with respect to water of crystallization. In the first examination of the crystallized sugar-cane amid it was found that the crystals, when well dried by pressing between filter-paper, did not lose weight during a short exposure to a temperature of 100° C. Subsequently it was found that the crystals, when finely powdered, lost water at 105°-110° C., and the average of several determinations, drying until there was no further loss in weight, gave 10.72 per cent. This, if we accept the formula $\text{CH}_2\text{NH}_2\text{COOH}$ as representing the molecule of glycocholl, is equivalent to half a molecule of water of crystallization. This was discovered too late to correct the error in my first paper.

The samples in which nitrogen was determined were in all cases finely powdered and dried at 110° C. so that 18.69, the per cent. of nitrogen stated, is that present in the amid after water of crystallization has been driven off.

The presence of water of crystallization in the sugar-cane amid of course invalidates my statement that it contains the