

kind with amused resignation and uses political party names merely as a nomenclature. He was in the lap of the gods and unaccustomed to question their decrees.

In 1885 Fischer visited Corsica. Passing through Paris, he dropped his gold watch on the boulevard, but returned after a few steps and picked it up. At Marseilles he demanded a few thousand francs on a letter of credit and had to wait because the bank was short. He informs us that the "vendetta" was still practised in Corsica and that a charming account of this barbarous custom is given in an excellent novel by Prosper Mérimée, entitled "Colomba." He omits to tell us, in connexion with his earlier visit to Denmark, that Shakespeare wrote "Hamlet."

Hundreds of great names flit through the pages of these recollections. With each one is associated some petty and often sordid detail. We are told that Graebe's horse-laugh attracted the attention of all the guests in the dining-room of the Grand Hotel in Territet and that Pechmann lost most of his fortune at Monte Carlo, but the master says no word in praise or appreciation of the services rendered by these two celebrated chemists in the development of their science.

It seems to be possible in Germany for an individual of great intellectual endowments to achieve eminence in some narrowly confined branch of science and still to remain ignorant of all those weighty matters which lie outside the limited domain in which he is supreme; this is perhaps responsible for much that has happened during late years. One of my friends recently visited a German scientific man of high standing and was informed by him that England must be in a desperate state; that we have so many unemployed living at the Government charge, that the State has boarded out great numbers of them in Austria because they can be maintained there at a less cost than in England. The statement must be true, because it has appeared in all the German newspapers! A similar detachment from human concerns led Fischer to sign the notorious manifesto of the 93 in September, 1914, justifying the violation of Belgian neutrality; a few years later he expressed regret at this ill-considered action.

The unfortunate impression made by Fischer's recollections was evidently foreseen in Germany, and the earlier part of Kurt Hoesch's life, published by the German Chemical Society, consists in a journalistic paraphrase of the recollections in which the trivialities are submerged under a flood of Teutonic sentimentality. Hoesch is astonished to find so little mention of the war of 1870, and explains it somewhat naïvely by saying that Fischer's character was an international one, and that he was a good European or, indeed, a super-European. "Aus meinem Leben" affords no support for this ingenious proposition.

NOTES ON THE DETERMINATION OF "MIXED ACID"

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Various methods have been employed for the analysis of "mixed acid," i.e., mixtures of nitric and sulphuric acids, such as are used in nitration, or the spent acid left after nitration. The present notes are based on experience in comparing known methods of analysis or modifications of them.

Total acid is easily determined by titration with standard caustic soda. The alkali is added from a burette to a weighed amount of the acid to be tested until a definite pink coloration is obtained in presence of phenolphthalein (the alkali being standardised under similar conditions). In another method the acid is added to a definite volume of the alkali in presence of methyl orange until a red colour is obtained, and the excess acid is titrated with caustic soda until the colour becomes pale yellow and finally turns pink after adding phenolphthalein.

Nitrous Acid.—For the separate determination of nitrous acid the well-known permanganate method is best, and it is satisfactory for fresh acid. With spent acids, in which the nitrous-acid content is high and organic matter is always present, titration with permanganate needs careful control. The method may be employed in analysing waste acid from TNT manufacture, containing matter not readily oxidised by permanganate. The influence of organic matter is shown by its effect on the end-point when the titration is performed at different temperatures up to 100° C. The method, however, is inapplicable to waste acids from the manufacture of picric acid, as oxalic acid is invariably present. Therefore some other method of estimating nitrous acid in presence of organic matter must be used, or other methods must be adopted which distinguish between the total nitrogen and the nitrogen in nitric acid. A useful method of estimating nitrous acid alone is to add the sample to be tested to a strong solution of potassium citrate, free from carbonate, in a Lunge nitrometer. The sample is washed in with more citrate solution, and a concentrated solution of potassium ferrocyanide added; the amount of nitric oxide evolved corresponds with the nitrous-acid content of the sample. This method tends to give low results.

The analysis of mixed acid also involves the determination of the total nitrogen acids, and the nitric or the sulphuric acid. Methods which are generally applicable, and which may also be used for nitrates or nitrites in most cases, can be tabulated as follows:—

Total Nitrogen Acids.—(1) Nitrometer method. (2) Reduction to nitric oxide by ferrous chloride in acid solution. (3) Reduction to ammonia by the Arndt method, the use of Devarda alloy, electrolytic reduction, etc. **Nitric acid:** (4) Direct titration with ferrous sulphate. (5) Nitron method [after elimination of nitrous acid]. **Sulphuric acid:** (6) By evaporating off the nitrogen-containing acids and titrating the sulphuric acid directly. **Nitric acid and sulphuric acid:** (7) By double titration with barium hydroxide and sodium carbonate.

Methods (3) and (5) are not discussed in this paper; most of the other methods have been so long in use that it is difficult to quote references to the original literature.

DETERMINATION OF TOTAL NITROGEN-ACIDS

(1) *The Nitrometer Method.*—The use of a calibrated nitrometer is usually held to give correct results, but large errors may occur if the apparatus is not manipulated correctly, and especially if a large number of tests has to be made. Emphasis is laid on this point because the author has experience of two large works where serious discrepancies were found in the results of routine estimations. Two nitrometers which nearly always showed large differences were examined and the divergence was found to be due to a difference in the tap-connexion which had led to different ways of using the nitrometers. An experiment which accentuates the error can be carried out as follows:—The nitric-oxide gas is expelled through the cup after an estimation has been made, and some of the acid lying on the mercury is allowed to enter the cup, thereby becoming exposed to the air. If this acid is drawn back into the nitrometer, or the walls of the cup are washed with pure sulphuric acid, and this is again shaken with the mercury, without adding any more nitrate, a further quantity of nitric oxide will be evolved which may amount to one-half the volume originally obtained. This production of gas can be repeated indefinitely and appears to be due to oxidation of the gas in contact with air to peroxide, which dissolves in the acid on the walls of the cup. A similar phenomenon may occur to some extent in the bore of the tap. Nitrometers should, therefore, always be constructed with a side-tube and cup connected by a two-way stopcock with two parallel diagonal bores (Greiner-Friedrichs cock). The gas can then always be expelled through the side tube, never through the cup, and each bore of the tap is used for one purpose only. About 5 c.c. of 90 per cent. sulphuric acid should be used with the sample in the nitrometer. Acid of greater strength must, according to Lunge, be avoided, and weaker acid gives a low result. A sample treated with sulphuric acid diluted to 50 per cent. gave as result 26.1 per cent. nitric acid, but when treated with the same amount of acid of 90 per cent. strength, 26.3 per cent. Also, with the more dilute acid, the action is slow at first and the mercury blackens and loses mobility.

(2) *Reduction to Nitric Oxide.*—The method of reducing to nitric oxide by ferrous chloride in acid solution, known as the Schlösing-Grandeau or Tiemann-Schulze method, has been modified by De Koninck and others (*cf.* Lunge-Berl., "Chemisch-technische Untersuchungsmethoden," 7te Auf. I., p. 783 *et seq.*). To compare this with other methods the following modification was used:—The ferrous chloride solution and the hydrochloric acid were boiled in a flask until free from air, and the flask was connected through a mercury seal with the gas-measuring tube, the drop of the delivery tube to the mercury being greater than the barometric height. The sample of acid to be tested was added to the flask by a tap-funnel. The volume of gas evolved may either be reduced to N.T.P. and calculated as nitric acid, or it may be compared with a standard volume of nitric oxide obtained from a known amount of pure nitrate or nitric acid. The two methods give slightly different results. Using spent acid and the nitrometer method, the results agreed within 0.05 per cent.; with fresh acid a result within 0.12 per cent. could be obtained by

careful measurement and correction of volume, but when an old standard volume is used the result may be too high by 0.2 per cent. or more. The liability to error is greatest in making a first estimation with a fresh charge of ferrous salt. It has been proposed to extend the method to the determination of nitrous acid (*cf.*, Meisenheimer and Heim, Ber., 38, 1905, p. 3834) by reduction to nitric oxide with potassium iodide; Raschig, Ber., 38, 1905, p. 3911), separate determination by titrating the free iodine in an atmosphere of carbon dioxide; (Strecker, Ber., 51, 1918, p. 997) estimating the nitrite in neutral solution as nitrogen, after decomposition with a very large excess of ammonium chloride. No attempt has been made to compare these methods with others mentioned.

DETERMINATION OF NITRIC ACID

(4) *Direct Titration with Ferrous Sulphate.*—It has often been doubted whether even approximate results can be obtained by this method, which dates at least from 1847. Bowman and Scott (Chemical News, 114, 1916, p. 39) showed that if properly carried out, it could safely be used for estimating nitric acid alone in presence of other acids (with some exceptions) or of nitrites. Since then a modification of the method has been shown to be capable of giving results agreeing within 0.1 per cent, with those obtained for nitric acid determined by the nitrometer, or for pure nitric acid estimated by direct titration.

The ferrous sulphate solution, made by dissolving the pure crystals in 30 per cent. sulphuric acid, is added directly from a burette, and the end-point is marked by the formation of the brown colour due to interaction between ferrous sulphate and nitric oxide. The conditions necessary to obtain results accurate within 0.1 per cent. are as follows:—(a) An excess of sulphuric acid must be used; hence the sample to be titrated, about 0.5 g., is mixed with about 100 c.c. of concentrated sulphuric acid. (b) The flask is kept at a temperature of under 30° C. in water and agitated during titration. (c) The factor of the ferrous sulphate solution is determined just before use by standardisation against a known amount of pure nitrate or nitric acid. This procedure eliminates most of the error due to change in volume of the ferrous sulphate solution (which has a large temperature-coefficient), error by different observers in judging the end-point, and also the error due to the small amount of solution necessary to give the end-point colour, i.e., to effect reduction to nitric oxide. A sharper end-point might be obtained if most of the colour due to formation of ferric salts were eliminated by titrating with stannous sulphate, containing some ferrous sulphate, in a neutral atmosphere.

DETERMINATION OF SULPHURIC ACID

(6) *By Titration after Evaporation of the Nitrogen Acids.*—This method, which is used on the ground of convenience, was carried out for purposes of comparison as follows:—About 1 g. of the sample was run into a porcelain evaporating-basin (diam. 7 cm.). After evaporating for at least 30 minutes on a water-bath, 1 c.c. of water was added, the liquid stirred with a small glass rod kept in the basin, and then heated for 15 minutes more. The sulphuric acid was then titrated, using methyl orange as indicator. Experiments showed that this

method could give almost correct results, but it was not always reliable, the sulphuric acid content being in some cases more than 0.5 per cent. too high.

DETERMINATION OF NITRIC AND SULPHURIC ACIDS

(7) *By Double Titration.*—This titration described by Langbein (*Z. angew. Chem.*, 13, 1920, p. 1227) may be slightly modified as follows:—Total acid is determined by titrating the hot or boiling solution with barium hydroxide, using phenolphthalein as indicator. A known amount of standard sodium carbonate is then added in excess, the precipitated barium sulphate and carbonate are filtered off, and the excess of sodium carbonate titrated with standard hydrochloric acid, using methyl orange to show the final end-point. This method gives low results for nitric acid, but it is speedy, and there is no error due to the precipitate passing through the filter paper. It is accurate enough for corrections in bomb calorimetry, for which purpose it was used by Langbein, or even for the determination of the sulphur content of a fuel, since under the conditions of combustion or explosion in compressed oxygen, sulphur is oxidised completely to sulphuric acid, and is found, together with nitric acid, in the liquid in the bomb.

ELECTROCHEMICAL DEVELOPMENTS IN ITALY

Industrial conditions in Italy are very different from those to which we are accustomed in Great Britain. The main problem which confronts the Italian technologist is the high price of fuel, due to the fact that home supplies are negligible; on the other hand he has abundant water power. These circumstances tend to promote chemical development along electrochemical lines, and as one consequence much attention has been devoted since the war to the production of electrolytic alkali. The development of this industry was hampered at first by the usual difficulty of finding an outlet for the chlorine, which is produced simultaneously, but this problem appears to have been solved successfully and on somewhat original lines, with the result that an interesting group of industries has been established. Some of these developments are described briefly in the following notes.

The imports of caustic soda into Italy are considerable, but have dropped from 19,844 metric tons in 1916 to 13,921 t. in 1921. The total internal consumption is about 22,000 t. per annum, of which only 5,943 t. was produced in the country in 1913. To-day the potential internal production, if all the works were working at full capacity, would approximately cover the demand.

At the Pomilio Electrochemical Works (*L'Elettrochimica Pomilio*) near Naples, caustic soda is produced in Pomilio-Giordani electrolytic cells in which the yield per unit of current is about 93–95 per cent. of the theoretical. There are three batteries of 100 cells each, and each cell takes 3000 ampères. The output per 24 hours is 10 tons of 100 per cent. NaOH, obtained as a solution of 120 to 140 g. per litre, which is worked up in the evaporators and fusion pots to soda lye of the commercial strengths 38–40° B_é. and 48–50° B_é. and to fused caustic of 72–74° English degrees. Under Italian conditions it is, of course, necessary

to reduce to a minimum the fuel charges for evaporation; by using electrically-driven heat-pump evaporators and so utilising the thermal energy of the fuel to the utmost the company has succeeded in reducing the coal required to evaporate each cubic metre of water in the production of 48 B_é. caustic lye to 16 kg., as compared with 48 kg. with multiple-effect vacuum pans, 210 kg. by heating with indirect steam, and 260 kg. by direct firing. Naturally this extreme economy of coal is only effected by the auxiliary use of electric current to the amount of approximately 230 kw. per cb.m. The caustic fusion pots are also of special type, coupled in parallel or in series, with tangential heating and recovery of the heat of the chimney gases which are said to reduce the fuel charges to 75 per cent. of those incurred by using pots of less recent type. The chlorine is used for the manufacture of bleaching powder, synthetic hydrochloric acid (for which purpose the hydrogen from the batteries is also utilised), sodium hypochlorite and zinc chloride; in future it is to be used for the production of potassium and aluminium chlorides, alumina and silica from the leucite of the volcanic rocks in the neighbourhood. The chlorine is also utilised in producing pure cellulose from hemp fibre and other raw materials. Three thousand tons of bleaching powder is produced yearly in leaden chambers; the hydrochloric acid plant has a capacity of 2000 t. per annum, and 160 t. per month has been actually obtained. The annual production of sodium hypochlorite is 2000 t., which is absorbed by local textile and other industries; and the output of 50 tons per month of zinc chloride is supplied to the State railways for the impregnation of sleepers.

The Pomilio company is now producing pure cellulose by the Cataldi process in a recently erected works, the output being 7 to 8 tons per day. In this manner an outlet has been found for the surplus chlorine, and the development is expected to have a very good future. The main raw material is hemp fibre, which is the dry residue from the beaten and macerated hemp plant. The annual production of this material in the Province of Naples is 25,000 tons. Hitherto this product has been used only on a small scale for fuel. The method of treatment is essentially Cross and Bevan's analytical method of estimating cellulose, adapted for industrial purposes, and consists in treating the fibre successively with dilute caustic alkali solution, moist chlorine, and again with dilute caustic alkali. The main precaution necessary on the manufacturing scale is careful regulation of the access of chlorine, as otherwise excessive heating takes place and the fibre is destroyed, or even charred. Large quantities of hydrochloric acid are evolved. Other raw materials are used instead of hemp, namely poplar wood, esparto and straw. The quantities required for the production of 100 kg. of poplar cellulose are: moist chlorine gas, about 28 kg.; coal about 15 kg.; bleaching powder (for subsequent bleaching) about 6 kg.; and sodium hydroxide, in dilute solution, 5 kg. To produce 10 tons of cellulose per day by this method only 50 workpeople are required and about 80 kw. of electric power. The amount of water required is not greater than in other processes. A plant of the above-mentioned output requires about 1500 sq. metres of covered floor-space. The above figures represent a maximum of