

XXVII.—*A New Process for the Volumetric Estimation of Cyanides.*

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THE processes at present in use for the volumetric estimation of cyanides by solution of silver and iodine requiring, as they do, the absence of such frequently-occurring substances as ammonia and alkalis, and depending on solutions prone to change, are in so far faulty; and as besides it is often desirable to estimate the cyanide in an alkaline solution already containing silver cyanide, I have considered that the description of a process (which I have used for some years), and which is interfered with by no commonly occurring bodies, may have some interest for this Society. The process is the converse of that for the estimation of mercury, of which I published an account (*Chem. Soc. Jour.*, June, 1873, vol. xxvi, p. 565) some years ago, and which has just received such complete confirmation (*Chem. Soc. Jour.*, December, 1877, vol. ii, p. 679) at the hands of Professor Tuson and Mr. Neison; in fact, it was the publication of their paper that induced me to write the present note. The process for the estimation of cyanogen in compounds depends on the anomalous behaviour of mercuric cyanide with alkalis; so that, if to an alkaline solution containing cyanogen a mercuric salt is added, no precipitate takes place until all the cyanogen is combined with mercury; that is to say, as long as the decomposition $2\text{KCN} + \text{HgCl}_2 = \text{Hg}(\text{CN})_2 + 2\text{KCl}$ goes on, all the mercury existing as cyanide is not affected by alkalis. The cyanide is dissolved in water, placed in a beaker on a black slab (or black velvet), rendered alkaline preferably with ammonia, and a standard solution of mercuric chloride is added in successive quantities, with frequent stirring, until a permanent bluish-white opalescence is produced. The end of the reaction is sharply marked, and half a drop of a centinormal solution is sufficient to produce a strong opalescence.

To test the accuracy of the process, as well as to find if other substances had any interfering action, a solution of potassic cyanide, containing 0.00651 gram per c.c. (decinormal), was prepared, and the strength checked by silver estimation. A decinormal solution of mercuric chloride was also prepared, containing 0.0271 of the chloride per c.c. A portion of this solution was reduced to half strength, that is, containing 0.01355 per c.c., so that one c.c. of this was equal to one c.c. of the cyanide. It was found that 20 c.c. of the cyanide gave a

perceptible opalescence, when a small fraction over 20 c.c. of the mercury solution had been added; the excess was less than $\cdot 03$ of a c.c. in an average of five estimations. To find how little would really show the turbidity, I prepared a centinormal solution, and reducing it to half strength, I found that 20 c.c. of the decinormal cyanide required 200.1 c.c. of the mercury solution to produce a decided opalescence; but that was the highest, other experiments requiring between $\cdot 05$ to $\cdot 08$ c.c. of excess. This indicates a quantity of $\cdot 0000651$ of the cyanide, or an error of $\cdot 05$ per cent. A large number of experiments were made on the action of alkaline sulphates, chlorides, and nitrates, but with the same result as Tuson and Neison have already shown. I also found that very large quantities of ammonium salts prevent the appearance of the opalescence when small quantities of cyanides have to be estimated; but as the above authors have shown that the interference begins only when 15 times more ammonium salt is present than of mercury, it will be seen that in ordinary chemical analysis such a state of affairs seldom arises. The kind of impurities in which I was more interested, however, were those present in samples of commercial potassic cyanide, principally potassic cyanate and thiocyanate, as caustic alkalis and alkaline carbonates are entirely without action. Solutions of the cyanate and thiocyanate were prepared, containing $\cdot 05$ gram per c.c., and the following experiments were tried. Cyanate: 20 c.c. of the cyanide were measured off, and 10 c.c. of the cyanate solution added; and after rendering alkaline with ammonia, mercuric chloride (decinormal half strength) was added, when it was found that a single drop over 20 c.c. caused an opalescence. Two other experiments were tried, using 20 c.c. and 50 c.c. of the cyanate; the two took 20.05 and 20.08 to produce an opalescence. The fractions were done by completing the process with centinormal solution: thus it will be seen that cyanic acid has no effect on the process. Three other experiments were done, using very dilute solutions, but still there was practically no effect. Thiocyanate: as before, 20 c.c. of cyanide and 10 c.c. of thiocyanate were rendered alkaline with ammonia and the mercury solution added. It took 20.2 c.c. of the mercury. Two others with 30 c.c. and 50 c.c. of thiocyanate respectively took 20.6 and 21 c.c. of mercury solution. I suspected that the thiocyanate could not be quite pure, so I recrystallised some of what had appeared to be pure salt, and I found that it now had no effect; three quantities of 20 c.c. each, with 10.30 and 50 c.c. of thiocyanate, taking 20.01, 20.04, 20.07 for the production of the opalescence. It will thus be seen that thiocyanic acid has also no effect upon this process. As it is often desirable to estimate cyanides in a solution containing silver, as in electro-platers' baths, I added silver nitrate to three quantities of cyanide solution in the following proportions:—

- I. To 20 c.c., a quantity not sufficient to cause a precipitate.
- II. „ just sufficient to cause a precipitate.
- III. „ a large excess.

On adding a little ammonia to I and dissolving the precipitates II and III in ammonia, each took a very small fraction over 20 c.c. of mercuric chloride solution to produce an opalescence. This shows that silver salts do not interfere with the process. It will thus be seen that we have now a process by which cyanogen in combination can be estimated accurately, even in the most complex mixtures; and as mercuric chloride can easily be obtained pure and keeps unaltered in solution, the process is one of great facility.
