

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

NOTES ON THE ESTIMATION OF CYANOGEN BY SILVER NITRATE, USING POTASSIUM IODIDE AND AMMONIA AS INDICATORS.¹

BY WILLIAM J. SHARWOOD.

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THE introduction of the “cyanide process” for extracting gold from its ores has given increased importance to the methods for determining cyanogen in alkaline cyanides. It is necessary to estimate rapidly the strength of the solutions used, and also of the spent solutions, in order to check losses and to show the amounts of additional cyanide requisite to fortify the spent liquors for further use.

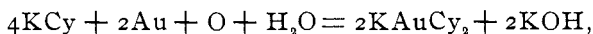
The best known volumetric methods are those of Liebig (by titration with standard silver nitrate until a permanent precipitate forms), and of Fordos and Gelis (with standard iodine); that of Hannay (titration with standard mercuric chloride in

¹ The essential part of this paper was read before the Chemical Section of the Science Association of the University of California, March 30, 1896. A number of observations on the delicacy of indicator, and on oxidizing agents, have been added since.

presence of ammonia till precipitate is permanent) is open to objection as the end is indistinct in presence of many commonly occurring impurities. The iodine method requires the neutralization of free alkali, and Liebig's method has been most generally used, both on account of its simplicity and the permanence of the standard solution; it is, however, slightly affected by certain common interfering substances.

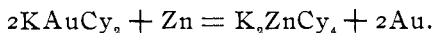
In the practical application of the "cyanide process," as usually carried out, the essential reactions are:

(I) For solution of the gold:



as was originally stated by Elsner, the necessity for the presence of free oxygen being disputed at first by MacArthur, but verified by MacLaurin.

(II) For precipitation by metallic zinc the equation usually given is:



Hence, starting with a solution of pure potassium cyanide, the spent liquors necessarily contain (beside the unaltered excess of potassium cyanide) potassium hydroxide, potassium zinc cyanide, and potassium zincate resulting from the solvent action of potassium hydrate upon zinc; the amount of zinc passing into solution is always far in excess of that calculated from the above equations on the basis of the gold precipitated. Owing to original impurities, to the decomposition of cyanide solutions in contact with the air, to incomplete precipitation, and especially to the action of various constituents of the ores treated (particularly sulphides in a more or less oxidized condition), there may also be present potassium aurous cyanide, potassium auric cyanide, potassium silver cyanide, mercuric cyanide, ferrocyanides, ferricyanides, double cyanides containing copper, nickel, or cobalt, (and probably manganese), cyanates, thiocyanates, sulphides, thiosulphates, ammonia compounds, oxamide, formates, etc., arsenites and antimonites (or their thio-salts), with sometimes very large quantities of calcium salts, and alkaline chlorides, sulphates, and carbonates. The potassium of commercial cyanide is often partly replaced by sodium, but without reducing its efficiency as a solvent for gold.

Caustic alkalis, alkaline plumbites, lime, soap, and certain oxidizing agents (as bromine, cyanogen bromide, mercuric chloride, and the peroxides of sodium and barium) are occasionally added during the process. The aim of the technical chemists has been primarily to estimate the simple alkaline cyanide, that existing in double cyanides having been considered "unavailable" for dissolving gold until recently, but certain double cyanides, especially that of zinc, have now been proved to have some solvent action.

Liebig's method gives accurately the cyanogen in solutions of alkaline cyanides, and of hydrocyanic acid after neutralization with soda or potash, the end-reaction consisting in a precipitation of silver cyanide; the addition of an alkaline chloride as indicator does not apparently affect the reaction. Cyanogen in mercuric cyanide, in cyanogen bromide, and in the double alkaline cyanides of silver, gold, nickel, cobalt, iron, copper, zinc, and a few other metals, cannot be estimated by it. Some of these substances, at least the two last mentioned metals, affect the determination of free alkaline cyanides to some extent. Solvents of silver cyanide, such as ammonia, ammonium carbonate, and thiosulphates, retard the end-reaction somewhat, giving high results; sulphides obscure it altogether by precipitating silver sulphide, and a large amount of free fixed alkali causes rather high results. Even in pure solutions the end is apt to be obscure or indefinite, a granular precipitate of silver cyanide forming and redissolving very slowly, making titration tedious. In presence of zinc (*i. e.*, pure potassium cyanide and pure potassium zinc cyanide) the end-reaction consists in the formation of a gelatinous precipitate of zinc cyanide soon after all the free or "available" alkaline cyanide has reacted. This "end" is rather vague, but is rendered sharper by addition of a little ferrocyanide as indicator, when a zinc ferrocyanide of doubtful composition falls out upon exhaustion of the uncombined alkaline cyanide; some of the cyanogen existing as double zinc cyanide is invariably reckoned in,¹ and this increases in presence of free alkali, so that the results of this so-called "available" cyanide

¹ Bettel (*Chem. News*, 72, 286, Dec. 13, 1895) states that exactly seven and nine-tenths per cent. of this is reckoned in. The writer has obtained variable results, averaging somewhat lower. Bettel himself mentions the time-effect and personal equation introduced.

titration are not strictly accurate. If enough caustic soda or potash be added to convert all zinc present into zincate *all* the cyanogen in the double zinc cyanide can be estimated ; but the end is not sharp and the excess of alkali modifies results appreciably. In practice a little ammonia may be present, retarding the end-reaction ; Mr. MacArthur appears to have been the first to suggest the use of potassium iodide as an indicator, the final precipitate being silver iodide, not appreciably affected by ammonia. Even with these improvements the end is not sharp and a precipitate is apt to form before reaction is complete, while time is a decided factor in titration when much zinc is present. The interference of soluble sulphides can be obviated by the method proposed by MacArthur, both for the estimation of cyanogen and as a metallurgical process, of adding lead carbonate or a solution of an alkaline plumbite and filtering off the lead sulphide formed.

In December, 1893, M. Georges Denigès¹ published a method of volumetrically estimating silver in any compound. He pointed out that none of the hitherto used volumetric processes for silver were universally applicable ; that Volhard's method with standard thiocyanate, though more general than Gay-Lussac's or Mohr's, could not be used with chlorides, bromides, or iodides of silver. He showed that every silver compound could be dissolved by means of potassium cyanide, or of ammonia and potassium cyanide (after a previous oxidation with nitric acid in the case of the metal, sulphide, and arsenide), without loss of cyanogen. He proposed to use a measured volume of a solution of potassium cyanide, in some excess of that required to form potassium silver cyanide with all the silver present, add ammonia and potassium iodide, and titrate with decinormal silver nitrate until a faint cloud of silver iodide forms ; then to titrate similarly an equal volume of the same cyanide solution with addition of ammonia and iodide ; the difference in the amounts of actual silver used in the two titrations equals the amount in the substance taken. The results quoted are perfectly concordant and accurate.

The present writer made at that time a few determinations of silver by this method, obtaining fair results, though less accu-

¹ *Compt. rend.*, 117, (26), 1078.

rate than with thiocyanate. Very satisfactory results were obtained in estimating iodide in presence of chloride, by precipitating with silver nitrate, treating with an excess of ammonia, washing the residue and redissolving it with potassium cyanide for titration. Some time later when estimating cyanogen by the method of Liebig, it struck the writer that an obvious corollary to Denigès' method for silver would be to apply his indicator, potassium iodide with addition of ammonia, to the determination of cyanogen; this was tried and very satisfactory results were obtained. The principal advantage found was in the rapidity of titration, the temporary precipitates dissolved instantly on shaking and the end was very sharp. In presence of zinc it was useless to attempt to determine "available cyanide;" increasing the ammonia indicated nearly all the cyanogen in potassium zinc cyanide, but never quite all unless fixed alkali were added. A number of experiments were then made to determine the accuracy of the method under varying conditions, more especially to ascertain the effect of the substances likely to occur in the liquors obtained in the MacArthur-Forrest and similar processes. Shortly after these were commenced, a second paper was published by M. Denigès, entitled "*Une nouvelle methode cyanométrique*,"¹ in which he recommends the use of the same indicator for estimating cyanides and quotes numerous experiments, mentioning that his attention was called to the use of an iodide indicator by a consideration of the relative thermal effects produced in precipitating silver as iodide and as cyanide. M. Denigès has therefore priority in the use of this indicator, his improvement consisting in the deliberate introduction of ammonia as well as an iodide. As the results published by Denigès covered but few of the substances occurring in spent cyanide solutions, these experiments were continued by the writer and a number of the results are here given. Many of the salts (such as those of the organic acids) were used merely with a view to their possible use in correcting the effect of other interfering substances more likely to be met with.

Regarding the solutions used: that of potassium cyanide was of approximately one-fifth normal strength, prepared from the "ninety-eight per cent." commercial cyanide of German make,

¹ *Ann. chim. phys.*, [7], 6, 381.

an analysis of which is given. Several liters of decinormal silver nitrate were prepared and the same solution was used through about half the experiments; later a twentieth-normal solution was found to be preferable, on account of the delicacy of the end-reaction. The silver solutions were prepared from metal 998.6 fine and were very carefully standardized by Volhard's method, and adjusted to the strength indicated by comparison with the purest silver obtainable.¹ The standard of the silver solutions was assumed not to vary during the experiments; actually a change of nearly one-tenth per cent. was found after several months, the solutions being kept in the dark. Potassium iodide was used in a five per cent. or three-tenths normal solution; two cc., containing one-tenth gram, were commonly taken. Commercial ammonia was used, of sp. gr. 0.93, corresponding to ten times normal strength; occasional determinations showed it to vary from ten to nine and one-half times normal strength; three to five cc. were usually added.

The burette used for the standard silver solution had a capacity of fifty cc. and was graduated to tenths; the back was white with dark stripe, enabling it to be read to one-fortieth cc., but ordinarily it was read to one-twentieth. The quantities of cyanide solution used were so adjusted as to require, normally, about twenty cc. of solution; they were always measured with the same pipettes, of ten and twenty cc. capacity. The burette was tested, and the errors in the first twenty cc. were found to be quite negligible; before each determination it was refilled, so as to obtain a reading from zero to about twenty cc., except in a few cases. The ordinary error of observation could not thus exceed one part in 400, and was more nearly one in 800. The glass stop-cock gave a drop slightly exceeding one-thirtieth cc., so that an extra drop would correspond to one part in about 600 of cyanogen present. The apparently greasy condition of the inner surface of the burette, which follows some days' use, was found to be completely remedied (after use with silver nitrate) by rinsing with a little weak solution of potassium cyanide.

The temperature of the laboratory ranged from 16° to 21° C.

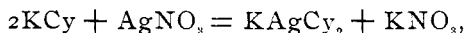
¹ This pure silver was prepared by reduction of fused chloride by pure zinc, and fusion of the washed metal, first with potassium bisulphate and then with borax; the chloride had been obtained by dissolving silver of a fineness of 998.6 in dilute nitric acid, filtering off the gold, precipitating from hot and highly dilute solution by hydrochloric acid, and repeatedly washing with hot water.

during observations, on only one or two occasions being 1° above or below these limits.

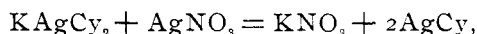
REACTIONS INVOLVED.

The reactions involved in the estimation of cyanogen by silver nitrate are :

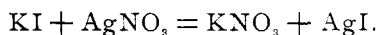
(1) Saturation, forming double silver cyanide :



and (2) precipitation of the excess of silver as *cyanide* :



or (3) as *iodide*, if an alkaline iodide be present :



The second reaction, but not the latter, being prevented by the presence of ammonium hydroxide or carbonate.

The terms "atom," "molecule," and "equivalent," as used in this paper in allusion to quantities of materials, refer to the corresponding weights expressed in *tenths of milligrams*, thus one cc. of tenth-normal silver nitrate contains one molecule silver nitrate, and corresponds in titration to two equivalents of cyanogen.

ANALYSIS OF "POTASSIUM CYANIDE 98 PER CENT."

	Per cent.	Corresponding to
Cyanogen.....	39.36	98.49 per cent. KCy.
Potassium	44.246	73.7 per cent. KCy.
Sodium	11.661	
Carbonic acid radical (CO ₂).....	3.57	6.31 per cent. Na ₂ CO ₃ .

Total determined..... 98.837

Traces of chloride, sulphate and ammonia were found, and a little water, but no indications of thiocyanates, cyanates, nor of iron in any form.

The association of base and acid was calculated as a check on the analysis, all the alkali-metal not combined being reckoned as hydroxide.

	Per cent.
Potassium cyanide.....	73.7
Sodium cyanide	18.68
Sodium carbonate	6.31
Sodium hydroxide.....	0.25
	98.94

As the alkaline cyanides are about equally efficient as solvents of gold, it is customary to report analyses as "percentage of potassium cyanide," based merely on the estimation of cyanogen; this is often misleading, a great part of the potassium being frequently replaced by sodium, as in the above case, so that nominally "100 per cent." potassium cyanide may contain ten or twenty per cent. of impurity; in fact pure sodium cyanide would be reported as 133 per cent. potassium cyanide, and a mixture of one gram-molecule each of sodium and potassium cyanides with sixteen grams of impurity would yield apparently 100 per cent. potassium cyanide, while containing over twelve per cent. of impurity. It would seem desirable to report the valuation of cyanides in terms of the "cyanogen contained in alkaline cyanides," or in some similar manner.

SERIES I.—COMPARISON OF RESULTS OBTAINED IN TITRATING POTASSIUM CYANIDE SOLUTIONS WITH STANDARD SILVER NITRATE BY THE METHODS OF LIEBIG AND DENIGÈS.

In each case the same (one-fifth normal) solution of potassium cyanide was used; in using Denigès' method five cc. of decinormal ammonia were added and one decigram of potassium iodide; each was titrated with silver nitrate of decinormal strength.

Set I.—By Liebig's method:

(a)	20 cc.	potassium cyanide solution	required	19.65 cc.	silver nitrate.
(b)	20 "	"	"	19.7 "	"
(c)	20 "	"	"	19.65 "	"
				Mean 19.667	"

Set II.—By the method of Denigès:

(d)	20 cc.	potassium cyanide solution	required	19.7 cc.	silver nitrate.
(e)	20 "	"	"	19.7 "	"
(f)	40 "	"	"	39.35 "	" or
(f)	20 "	"	"	19.675 "	"
				Mean 19.692	"

SERIES 2.—EFFECT OF VARYING VOLUME OF SOLUTION.

Using twenty cc. fifth-normal potassium cyanide solution, five

cc. ammonia, and one-tenth gram potassium iodide and adding water to make final volume 50 cc. or 150 cc.

(a)	20 cc.	diluted to 50 cc.	required	19.70	cc.	tenth-normal silver nitrate.
(b)	20 cc.	"	50 "	"	19.70	" " "
(c)	20 cc.	"	150 "	"	19.75	" " "
(d)	20 cc.	"	150 "	"	19.70	" " "

SERIES 3.—PROPORTIONALITY OF SILVER NITRATE USED TO CYANIDE PRESENT.

The potassium cyanide was added from a ten cc. pipette. Three cc. ammonia and one-tenth gram potassium iodide were used.

10 cc.	potassium cyanide solution required	9.8	cc.	silver nitrate.
20 "	" " " " " "	19.6	"	" " "
30 "	" " " " " "	29.4	"	" " "

SERIES 4.—EFFECT OF VARYING THE PROPORTIONS OF THE INDICATORS: POTASSIUM IODIDE AND AMMONIA.

The ammonia water was of approximately ten times normal strength.

Set I.—Varying potassium iodide, ammonia constant; using twenty cc. fifth-normal potassium cyanide, and five cc. ammonia.

Grams potassium iodide added.....	0.05	0.1	0.25	0.5
cc. tenth-normal silver nitrate required.	19.7	19.7	19.75	19.7
" " " " " "	19.75	19.7	19.7
" " " " " "	19.7	19.75	19.7
" " " " " "	19.7

Set II.—Varying both ammonia and potassium iodide. Using twenty cc. fifth-normal potassium iodide solution at a temperature of about 20° C.

Grams potassium iodide added.....	0.1	0.5	0.5	0.5
cc. ammonia added.				
5	19.7	19.75	19.7	19.7
10	19.8	...	19.75
20	19.85
30	19.9
55	20.2	20.1

Set III.—Using ten cc. of another fifth-normal solution of potassium cyanide at a temperature of 14° C.

Grams potassium iodide added.....	0.1	0.1	0.25	1.0
cc. ammonia added.	cc. twentieth-normal silver nitrate required.			
0	20.02	20.05	20.05
2	20.15
5	20.05	20.05
15	20.1
20	20.13	20.18
30	20.25
40	20.25
50	20.5	20.55	20.25

SERIES 5.—EFFECT OF VARYING TEMPERATURE.

Set I.—Using twenty cc. fifth-normal potassium cyanide solution, five cc. ammonia, and one-tenth gram potassium iodide.

Temperature	22°	45°	72°
cc. decinormal silver nitrate required	19.7	19.85	20.0

Set II.—Varying temperature and varying ammonia. Using ten cc. fifth-normal potassium cyanide and one-tenth gram potassium iodide, titrating with twentieth-normal silver nitrate.

Temperature.....	20°	48°	80°
cc. of tenth-normal ammonia added.	cc. tenth-normal silver nitrate added.		
5	(a) 20.05	(a) 20.2	(a) 20.3
5	(b) 20.05
15	(b) 20.1	..	(b) 20.8
20	(b) 21.1

In the last set of experiments the solution was warmed, or ammonia added, or both, until the end-precipitate from one determination had redissolved; silver nitrate was then added, drop by drop, until the precipitate reappeared.

From the preceding figures it seems that moderate variations in the proportions of indicators have but little effect on the results of estimating cyanogen by this method; it is, however, evidently desirable to keep the temperature constant, and to avoid an undue excess of ammonia which gives results somewhat too high.

In presence of a large amount of ammonia the error may be reduced somewhat by adding a larger amount of potassium iodide, but under ordinary conditions one-tenth gram is sufficient.

SERIES 6.—DELICACY OF INDICATOR.

Set I.—(a) With five cc. ammonia and one-tenth gram potas-

sium iodide, in fifty cc. water, no cyanide being added, one drop (or 0.03 cc.) of twentieth-normal silver nitrate was sufficient to give a very decided cloud of silver iodide. Using the same quantities of ammonia and iodide in 150 cc. of water, the same amount of silver salt gave a decided cloud, though of course less dense than in the smaller volume of liquid.

(b) With fifty cc. of a very dilute solution of sodium chloride, and adding five cc. ammonia and one-tenth gram potassium iodide, one drop of twentieth-normal silver nitrate gave a similar precipitate. In a similar solution, without these indicators, three to four drops were necessary to give an equally dense cloud.

(c) Taking forty cc. of a ten per cent. solution of sodium chloride, one drop of twentieth-normal silver nitrate gave a precipitate as heavy as in the preceding case, when ammonia and iodide were added. In an equal amount, without the indicator, three drops were necessary to give a permanent cloud, and four or five to render it as heavy as with the indicator.

(d) So also in forty cc. of a five per cent. solution of ammonium chloride, with ammonia and iodide, one drop of twentieth-normal silver nitrate gave a similar cloud; without the indicator, one drop gave a faint opalescence, two gave about the same effect as one gave with iodide present.

Owing to the fact that no permanent precipitate is formed in presence of the slightest excess of alkaline cyanides, it was impossible to strictly compare the delicacy of the end-reaction with and without the iodide indicator. As the difference seemed to lie rather in the colors than in the solubilities of silver iodide and cyanide, it was thought that a comparison of the iodide and chloride might give approximately the same results. The following tests were all made with fifty cc. of distilled water, in flasks of about 120 cc. capacity.

Set II.

	Amounts present.			Silver nitrate solution added.	Effects of silver added.
	Sodium Chloride.	Potassium Iodide.	Ammonia.	(Twentieth normal from burette.)	
	Gram.	Gram.	cc.		
(a)	0.1	0.1	3	1 drop (0.035)	Decided cloud.
(b)	0.1	0.1	0	1 "	Cloud, slightly less dense than in (a).
(c)	0.1	0.0	0	1 "	Opalescence.
				2 "	Cloud, as dense as (a).

Set III.

	Amounts present.			Silver nitrate solution added. (One-hundredth normal from Mohr pipette.)	Effects of silver added.
	Sodium chloride. Gram.	Potassium iodide. Gram.	Ammonia. cc.		
(a)	0.1	0.1	3	0.1 cc.	Slight opalescence.
				0.2 "	Decided "
(b)	0.1	0.1	0	0.13 "	Faint "
				0.2 "	Decided "
(c)	0.1	0.0	0	0.1 "	Very faint "
				0.6 "	Precipitate equal in opacity to (a) with 0.2 cc.

Set IV.

(a)	0.1	0.1	3	0.12 cc.	Decided opalescence.
(b)	0.1	0.1	0	0.22 "	" " equal to (a).
(c)	0.1	0.0	0	0.15 "	Faint opalescence.
				0.29 to 0.35 cc.	" " equal to (a).

Set V.

(a)	0.1	0.1	3	1 drop (0.04 cc.)	Opalescence, slightly more than in (c) with one drop.
				2 "	Opalescence greatly increased.
(b)	0.1	0.1	0	1 "	Opalescence less than (a) or (b) with one drop.
				2 "	Opalescence increased, much less than (a) but more than in (c) with second drop.
				4 "	Opalescence equal to (a) with two drops.
(c)	0.1	0.0	0	1 "	Opalescence.
				2 "	" very slightly increased.
				6 "	Opalescence almost equal to (a) with two drops.

Set VI.—Identical with V, but made in reverse order.

Sets II, III, and IV were carried out in diffused light on a rather dull day; sets V and VI on a bright day, the flasks being held momentarily in direct sunlight for comparison. As

the appearance varies slightly with time, Set V was repeated in reverse order (VI), but the results did not apparently differ. In sets V and VI the effect of time was closely noticed; after standing five minutes the precipitate in (a), at first practically equal to the others, was appreciably heavier; after ten minutes that in (c) was evidently increasing; after one and two hours that in (c) was by far the most dense, (b) next, and (a) somewhat less dense than (b), proportionally to the amount of silver nitrate added to each.

It seems remarkable that the addition of ammonia should increase the delicacy of the iodide precipitation of silver, but the results in all the last five sets of tests indicate that this is the case, at least within a few minutes of the precipitation, the time when the sensitiveness of an end-reaction is of most value. The addition of ammonia has therefore the unexpected advantage of rendering the end still sharper than it is with potassium iodide alone, as well as of redissolving the temporary precipitates more rapidly than the cyanide does when nearing the end of titration, while the use of the simple iodide indicator is preferable to the ordinary "Liebig" method, chiefly on account of the yellowish color of the silver precipitate, this being more readily visible than silver chloride or cyanide, either with a dark or light background.

Effect of Indicator in Presence of Considerable Proportions of Alkaline Ferrocyanides, Ferricyanides, Thiocyanates, and Thiosulphates.

As the above salts in quantity caused some variation in the amounts of cyanide found by titration, the following tests were made with a very dilute (one hundredth-normal) solution of silver nitrate, to ascertain the extent to which they dissolved silver iodide, and the readiness with which they themselves precipitated silver from the nitrate.

Set VII.—The volume of liquid was in each originally twenty-five cc., no cyanide being taken.

Salt taken.	NH ₄ CNS.	K ₄ FeCy ₆ .	K ₃ FeCy ₆ .
Grams of salt added (crystals)	1.9	1.09	0.825
Molecules " " "	250.0	25.0	25.0

cc. hundredth-normal silver nitrate required to precipitate :

(a) With one-tenth gram potassium iodide and three cc. ammonia as indicator	0.85	0.75	0.4
(b) Without indicator.....	{ over 10.0 ¹	1.0	about 0.5
Equivalents of cyanogen corresponding to silver used with iodide indicator.....	0.17	0.15	0.08
Molecules potassium cyanide to give same effect as one molecule of salt, with indicator.....	0.0007	0.006	0.003

Set VIII.—Using one-tenth gram of crystallized sodium thio-sulphate (4 molecules) in twenty-five cc. water, no cyanide being added.

	(a)	(b)	(c)	(d)
Indicator used.....	none.	0.1 gr. NaCl.	0.1 gr. KI.	0.1 gr. KI+3 cc. NH ₄ OH.
cc. twentieth-normal silver nitrate required to give a precipitate	over 10; (solution blackens.)	6.4	0.15	0.1
Molecules potassium cyanide to give same effect as one molecule sodium thiosulphate	?	1.6	0.04	0.025
Molecules sodium thiosulphate to give same effect as one molecule potassium cyanide	?	0.625	27.0	40.0

The use of ammonia and iodide as an indicator is therefore of great advantage in presence of thiocyanates and thiosulphates, but of only slight advantage in presence of ferrocyanides, and makes little difference with ferricyanides.

SERIES 7.—EFFECT OF FIXED CAUSTIC ALKALI.

Set I.—Using twenty cc. fifth-normal potassium cyanide solution, five cc. ammonia and one-tenth gram potassium iodide :

cc. of two per cent. solution of sodium hydroxide added	0.0	50.0	100.0
cc. of tenth-normal silver nitrate solution required	19.7	19.7	19.7

Further additions of 50 and 100 cc. of soda solution did not appreciably affect precipitate.

Set II.—Using five cc. fifth-normal potassium cyanide, added to forty cc. water.

¹ Required 12.3 cc. of twentieth-normal.

Potassium hydroxide added.....	none	4 grams
		cc. twentieth-normal silver nitrate required.
(a) By Liebig's method, without indicator	9.75	10.9
(b) By Denigès' method, with three cc. ammonia and one- tenth gram potassium iodide.....	9.75	9.8

A more extended series of comparisons is quoted by Denigès.

SERIES 8.—EFFECTS OF VARIOUS SALTS.

In these determinations the salts were either weighed out directly, dissolved and added, or were measured out from roughly standardized solutions. Approximately fifth-normal potassium cyanide solution was used, ten cc. being usually taken, with three or five cc. ammonia, and one-tenth gram potassium iodide as indicator. The approximate numbers of molecules of each salt, associated with twenty molecules of potassium cyanide, is given in column 3. The numbers of equivalents of cyanogen, given in columns 4 and 5, were taken as equal to the numbers of cc. of twentieth-normal silver nitrate consumed, those of column 4 being daily checked.

Substance added.	Grams.	Molecules.	Equivalents of K Cy taken.	Equivalents of Cy found by titration.	Difference.	Percentage error.
Sodium chloride.....	2.4	400.0	20.0	19.9	0.1	+0.5
“ “	4.0	680.0	19.8	19.85	0.05	+0.25
“ “	4.0	680.0	19.8	19.8	0.0	0.0
Sodium sulphate (cryst).	6.5	200.0	20.0	0.0	0.0	0.0
Sodium carbonate (cryst)	1.43	50.0	20.05	20.1	0.05	+0.25
Sodium carbonate (cryst. = 0.53 gram anhy- drous)	1.43	50.0	20.05	20.0	0.05	-0.25
Potassium nitrate.....	1.05	100.0	20.05	19.9	0.15	-0.75
“ “	5.2	500.0	19.8	19.7	0.1	-0.5
Ammonium chloride....	1.2	220.0	20.0	19.8	0.2	-1.0
“ “	1.8	330.0	19.8	19.8	0.0	0.0
“ “	3.0	550.0	19.8	19.8	0.0	0.0
Disod. phosphate (cryst)	1.43	40.0	20.0	±20.0 ¹	±0.2	±1.0
Disod. phosphate (+0.5 gram NaOH).....	1.43	40.0	20.0	±20.0 ¹	±0.2	±1.0
Microcosmic salt.....	4.2	200.0	20.0	19.8	0.2	-1.0

Substance added.	Grams.	Molecules.	Equivalents of KCy taken.	Equivalents of Cy found by titration.	Difference.	Percentage error.
Sodium sulphite ($7H_2O$)	2.5	100.0	20.0	19.95	0.05	-0.25
Potassium chlorate.....	1.0	80.0	20.0	20.0	0.0	0.0
Potassium dichromate (titrated immediately).....	0.125	4.2	20.0	20.1	0.1	+0.5
Potassium dichromate (titrated after ten minutes).....	0.44	15.0	20.15	20.2	0.05	+0.25
Potassium dichromate (titrated after one hour).....	0.44	15.0	20.15	19.85	0.30	-1.5
Ammonium oxalate.....	1.07	75.0	20.0	20.0	0.0	0.0
Sodium formate.....	2.75	320.0	20.0	20.0 ¹ to 20.05	0.0 to +0.05	0.0 to +0.25
Acetic acid (glacial, neu- tralized by soda)....	3.0	500.0	20.0	19.9	0.1	-0.5
Citric acid (neutralized by soda).....	3.0	140.0	20.0	20.0	0.0	0.0
Tartaric acid (neutralized by soda).....	3.0	250.0	20.0	20.0	0.0	0.0
Arsenious oxide (+excess NaOH).....	0.132	7.0	20.0	20.1	0.1	+0.5
Arsenious oxide(+excess NaOH).....	0.132	7.0	20.0	20.15	0.15	+0.75
Sodium arsenite (Na_2H- AsO_3 anhydrous)....	1.0	0.0	20.0	20.05	0.05	+0.25
Potassium antimonite ...	2.0	...	19.8	19.8 to 19.9	0.5 to 0.1	+0.25 to +0.5
Potassium stannate.....	2.0	...	19.8	19.85	0.05	+0.25
Sodium plumbite (Pb 0.105 gram).....	..	5.0	19.8	19.5	0.3	-1.5
Sodium plumbite (Pb 0.105 gram + excess NaOH).....	..	5.0	19.8	19.7	0.1	-0.5
Sodium plumbite (Pb 0.207 gram + excess NaOH).....	..	10.0	19.8	19.7	0.1	-0.5
Sodium silicate.....	2.0	...	19.8	19.7 ¹	0.1	-0.5
Borax.....	4.0	100.0	10.05	10.05	0.0	0.0
Barium chloride (cryst.)	1.85	75.0	19.8	19.75-19.85	± 0.05	± 0.25
Calcium chloride(anhyd)	2.78	250.0	20.0	19.95-20.05	± 0.05	± 0.25

¹ End not sharp.

Substance added.	Grams.	Molecules.	Equivalents of KCy taken.	Equivalents of Cy found by titration.	Difference.	Percentage error.
Potassium alum.....	2.8	60	20.0	19.95	0.05	-0.25
(with sodium hydroxide).....	(0.32)	(80)				
Chrome alum (with sodium hydroxide)....	0.25	5.0	16.0	16.05	0.05	+0.3
Chrome alum (with sodium hydroxide)....	3.0	60.0	19.8	19.2	0.6	-3.0
Magnesium sulphate crystals, with ammonium chloride.	2.0	80.0	20.05	20.1	0.05	+0.25
	0.36	66.0				
Ammonium thiocyanate.	0.152	20.0	19.7	19.6	0.1	-0.5
" "	0.152	20.0	19.8	19.7	0.1	-0.5
" "	0.152	20.0	19.8	19.75	0.05	-0.25
" "	1.6	200.0	19.8	19.8	0.0	0.0
" "	1.6	200.0	19.8	19.85	0.05	+0.25
Potassium ferrocyanide..	0.17	4.0	39.4	39.5	0.1	+0.25
" "	2.18	50.0	19.8	19.9	0.1	+0.5
" "	2.18	50.0	19.8	19.9	0.1	+0.5
" "	2.18	50.0	10.05	10.15	0.1	+1.0
Potassium ferricyanide..	0.132	4.0	19.7	19.7	0.0	0.0
Potassium ferricyanide (solution two weeks old)	0.658	20.0	20.15	19.2	0.95	-4.9
Potassium ferricyanide (new).....	0.658	20.0	20.15	20.0	0.15	-0.75
Potassium ferricyanide (new with NaOH) .	0.658	20.0	20.15	19.6	0.55	-2.7
			to 19.9	to 0.25	to -1.25	
Potassium ferricyanide (new with NaOH). .	0.658	20.0	10.05	9.95	0.1	-1.0
Sodium thiosulphate....	0.25	10.0	20.1	20.95	0.85	+4.2
Sodium thiosulphate....	0.5	20.0	20.1	21.8	1.7	+8.5
Alcohol (50 cc., pure 50 per cent.).....	20.1	20.1	0.0	0.0
Alcohol (100 cc., commercial 50 per cent.)	20.1	20.3	0.2	+1.0
Cane sugar	5.0	...	19.8	19.8	0.0	0.0
Soap.....	0.25	...	19.8 ¹	19.75-19.85	±0.05	±0.25

It will be seen that relatively large proportions of salts were

¹ End not sharp.

added in most of the experiments quoted: numerous other experiments were made with smaller quantities, the effects of which were generally quite negligible. The effects of oxidizing agents, and of salts of metals forming double cyanides (generally proportional to the amounts added), and of thiosulphates and sulphides, are given in other series. Nitrates generally give somewhat low results. Salts of aluminum, chromium, and magnesium interfered greatly unless kept in solution by fixed alkali or sal ammoniac respectively. With chromium the end-reaction can be clearly seen by looking through a thin layer of the green liquid at a white object. Calcium salts render the end indistinct by precipitating as carbonates; this is partially remedied by sal ammoniac. Iron salts gave precipitates when added, and the results of subsequent titration were most irregular; attempts were made to retain the iron in solution by addition of organic acids, followed by excess of alkali; in some instances this was entirely successful, but generally the results were low and variable, and were not thought worth tabulating.

The stannates and salts of their class were studied with a view to their possible use to prevent the interference of sulphides; they generally give somewhat high results, while those with plumbites are a trifle low. In presence of phosphates the end is somewhat uncertain, and similarly with large proportions of sodium carbonate and chloride; such solutions should be diluted and the silver solution added slowly.

Moderate additions of thiocyanates gave slightly low results; with very large amounts, results are normal or very slightly high. Ferrocyanides gave rather high results, the percentage error increasing fairly regularly with the ratio of ferrocyanide to simple cyanide. With ferricyanides the results were low, but irregularly low; additions of ammonia or fixed alkali seemed rather to increase the irregularity; time affected the interference of ferricyanides, and the final precipitate increased greatly on standing. The interference of small proportions of the three last-mentioned salts,¹ such as met in working solutions, would be ordinarily negligible. Their effect on the indicator is shown in series 6, set VII, that of thiosulphates in set VIII.

¹ For a discussion of the interference of these salts with the iodine and Liebig methods of titration, see J. E. Clennell, *Chem. News*, 5, 72, 1882.

SERIES 9.—EFFECTS OF ZINC.

The zinc was added in the form of a solution of the chloride, containing 0.0099 gram metal per cc. (1 cc. = 1.52 atoms zinc).

The series of results, indicated in any vertical column, were obtained by adding ammonia (or, in some cases, sodium hydroxide or ammonium chloride) in sufficient quantity to redissolve the precipitates formed, and then continuing the titration until a further precipitation occurred.

Effect of Varying Zinc and Ammonia.

Set I.—Using twenty cc. fifth-normal potassium cyanide solution (containing 39.4 equivalents Cy), and one-tenth gram potassium iodide.

Zinc added—grams	0.0	0.0198	0.0495	0.099
Zinc added—atoms	0.0	3.04	7.6	15.2
Ammonia added, ten times normal. cc. (Mols.)	*	cc. tenth-normal silver nitrate required.		Diff.
		Diff.	Diff.	Diff.
5 (500)	19.7	18.8 (0.9)	16.85 (2.85)	12.65 (7.05)
10 (1000)	19.75	19.3 (0.45)	18.15 (1.6)	16.3 (3.45)
15 (1500)	19.8	19.45 (0.35)	18.7 (1.1)	17.55 (2.25)
20 (2000)	19.85	same	19.0 (0.85)	18.2 (1.65)
25 (2500)	19.9	19.2 (0.7)	18.6 (1.3)
30 (3000)	19.95	same	18.8 (1.15)
35 (3500)	20.0	19.0 (1.0)
40 (4000)	20.5	same

Set II.—Using ten cc. fifth-normal potassium cyanide solution (containing 20.05 equivalent Cy), and one-tenth gram potassium iodide, adding 0.0297 gram zinc (4.56 atoms) in each case.

Ammonia added, ten times normal. cc. (Mols.)		cc. tenth-normal silver nitrate required.	Differ- ence from 10.03
1 (100)		1.15	(8.88)
3 (300)		8.55	(1.48)
5 (500)		9.0	(1.03)
7 (700)		9.25	(0.78)
9 (900)		9.5	(0.53)
11 (1100)		9.6	(0.43)
11 (1100) + 0.08 gram NaOH = 20 molecules		9.8	(0.23)
11 (1100) + 0.16 gram NaOH = 40 molecules		9.95	(0.08)

Throughout the series of experiments with zinc and ammonia the precipitates (which appeared to consist of zinc cyanide)

* Some of the numbers in this column were obtained by interpolation.

redissolved on standing a short time; the titrations were therefore performed by adding the silver nitrate solution drop by drop, increasing the interval to about a quarter of a minute as the "end" approached; the numbers given indicate the least volumes which gave a precipitate that was permanent for about a minute.

Effects of Zinc in Presence of Ammonium Chloride and Ammonia.

Set III.—Using ten cc. fifth-normal potassium cyanide solution (containing 20.05 equivalents Cy), and one-tenth gram potassium iodide, adding 0.0297 gram zinc (4.56 atoms) in each case.

Ammonia added, ten times normal.		Ammonium chloride added.		cc. tenth-normal silver nitrate added.	Diff. from 10.03.
cc. (Mols.)	Gms. (Mols.)	(Mols.)			
1 (100)	0.6 (110)	3.5	slight precipitate, redissolves slowly.		(6.53)
1 (100)	0.6 (110)	4.0	" " " "		(6.03)
1 (100)	0.6 (110)	5.0	" " permanent two minutes.		(5.03)
3 (300)	1.2 (220)	8.5	" " " " " "		(1.53)
5 (500)	1.2 (220)	9.0	" " " " " "		(1.03)
7 (700)	1.2 (220)	9.3	" " permanent.		(0.73)

A comparison of the last two tables shows that ammonium chloride has but little effect in preventing the interference of zinc compounds, as compared with ammonia, while caustic soda is far more effective than either.

When little or no ammonia is added the number of equivalents of cyanogen, retained by one atom of zinc, approaches four, but never reaches it. The first additions of ammonia greatly reduce the ratio of cyanogen to zinc; larger additions have a less proportionate effect, but gradually bring the cyanogen combined by the zinc to near zero.

Effect of Zinc in Presence of Caustic Soda.

Set IV.—Using in each case twenty cc. fifth-normal potassium cyanide solution, with varying amounts of zinc chloride and varying amounts of four-tenths normal solution of caustic soda, adding to each five cc. ammonia and one-tenth gram potassium iodide.

Zn added—grams	0.0	0.198	0.0495	0.099	0.198	
Zn added—atoms	0.0	(3.0)	(7.6)	(15.2)	(30.4)	
Sodium hy- droxide solu- tion added.						
cc. (Mols.)	Gms.	cc. tenth-normal silver nitrate required.				
		Diff.	Diff.	Diff.	Diff.	
0	0	19.8	18.85 (0.95)	16.9 (2.9)	12.4 (7.4)	0.0 (?)
10	(40)	19.8	19.75 (0.05)	19.7 (0.1)	17.5 (2.3)	8.85 (11.25)
20	(80)	19.8	19.8 (0.0)	19.5 (0.3)	15.1 (4.7)
30	(120)	19.8	19.6 (0.2)	19.4 (0.4)
40	(160)	19.8	19.6 (0.2)

Additions of caustic soda, further than those indicated, failed to redissolve the end-precipitate. It is evident that the interference of zinc is minimized when the number of molecules of caustic soda added exceeds four times the number of atoms of zinc present.

SERIES 10.—EFFECT OF COPPER.

Copper was added as a solution of the nitrate, containing 0.005 gram metal per cc. (1 cc. = 0.79 atom copper); 0.1 gram potassium iodide was added in each case.

Varying Copper and Ammonia.

Set I.—Using twenty cc. fifth-normal potassium cyanide solution containing 39.6 equivalents of cyanogen.

Copper added—grams	0	0.025	0.05	0.075	
Copper added—atoms	0	3.95	7.9	11.85	
Ammonia added ten times normal.					
cc. (Mols.)	Gms.	cc. tenth-normal silver nitrate required.			
		Diff.	Diff.	Diff.	
5	(500)	19.8	13.0 (6.8)	6.2 (13.6)	1.2 (18.6)
10	(1000)	19.85	13.2 (6.65)	6.55 (13.3)	1.2 (18.65)
15	(1500)	19.9	13.3 (6.6)	6.8 (13.1)	2.2 (17.7)
20	(2000)	19.95	13.4 (6.55)	7.05 (12.9)	2.65 (17.3)
25	(2500)	20.0	same	7.25 (12.75)	2.85 (17.15)
30	(3000)	20.05		same	3.15 (16.9)

Equivalents of cyanogen combined by one atom of copper 3.43 to 3.3, 3.43 to 3.22, 3.18 to 2.85.

Time affected results somewhat; the precipitates slowly cleared.

Effect of Copper in the Presence of Caustic Soda.

Set II.—Using twenty cc. of fifth-normal potassium cyanide solution (containing 39.6 equivalents Cy), with five cc. ammonia and one-tenth gram potassium iodide, adding 0.05 gram copper as nitrate (7.9 atoms copper).

Sodium hydroxide added.	cc. tenth-normal silver nitrate required.	Diff.
none	6.2	(13.6)
0.32 gram (80 mols.)	6.3 to 6.35	(13.5)

A temporary black precipitate formed on each addition of silver solution, rendering the end rather indistinct.

SERIES II.—EFFECT OF CADMIUM, VARYING CADMIUM AND AMMONIA.

Cadmium was added as a solution of the nitrate, containing 0.03 gram metal per cubic centimeter (1 cc. = about 2.6 atoms cadmium).

Ten cc. fifth-normal potassium cyanide solution were used in each case, with one-tenth gram potassium iodide.

Cadmium added—grams	0	0.06	0.12	0.12*	0.3
Cadmium added—atoms	0	5.2	10.0	10.0	26.0

Ammonia added ten times normal.			cc. tenth-normal silver nitrate required.		
cc.	(Mols.)	Gms.	Diff.	Diff.	Diff.
3	(300)	10.05	7.4 (2.65)	..	7.0 (3.05) ..
4	(400)	10.05		8.4 (1.65)	..
6	(600)	10.05	8.6 (1.35)	9.0 (1.05)	9.3 (0.75)
8	(800)	10.05			
10	(1000)	10.05			
14	(1400)	10.05			
18	(1800)	10.05			

The end-point was very indefinite in presence of cadmium; neither ammonium hydroxide nor the chloride affected the irregularity of the final precipitates, which sometimes slowly cleared and at other times greatly increased on standing. In several other experiments, with smaller amounts of cadmium, the interference was practically avoided by a considerable addition of ammonia. Caustic soda was without effect.

SERIES I2.—INTERFERENCE OF VARIOUS METALS FORMING SOLUBLE DOUBLE CYANIDES.

Metal.	Gram metal added.	Atoms metal added.	Equivalents KCy taken.	Equivalents Cy found by titration.	Difference (= equivalents of Cy combined).	Equivalents Cy combined per atom of metal.
Gold—as HAuCl_4Aq	0.018	0.914	25.0	21.1	3.9	4.27
as KAuCl_4Aq	0.018	0.914	25.0	21.3	3.7	4.05
as HAuCl_4Aq	0.09	4.57	39.4	20.6	18.8	4.11

* Ammonium chloride (0.33 gram = 60 mols.) was added in this case.

Metal.	Gram metal added.	Atoms metal added.	Equivalents KCy taken.	Equivalents Cy found by titration.	Difference(=equiv- alents of Cy com- bined).	Equivalents Cy combined per atom of metal.
Gold—as HAuCl_4Aq	0.18	9.14	39.4	2.1	37.3	4.08
as HAuCl_4Aq	0.025	1.24	24.9	20.0	4.9	3.99
as HAuCl_4Aq	0.02	1.01	19.8	15.9	3.9	3.86
as HAuCl_4Aq	0.04	2.03	19.8	11.8	8.0	3.94
as HAuCl_4Aq	0.07	3.55	19.8	5.75	14.05	3.98
as HAuCl_4 large excess						
NaOH.....	0.02	1.01	19.8	18.1	1.7	1.7
as metal "leaf".....	0.030	1.523	39.0	35.9	3.1	2.03
" ".....	0.03826	2.99	19.8	13.05	6.75	2.28
" ".....	0.07715	3.916	19.8	10.25	9.65	2.44
Mercury--as HgCl_2Aq	0.1	5.0	19.8	9.1	10.7	2.14
as $\text{Hg}(\text{NO}_3)_2\text{Aq}$	0.05	2.5	19.8	14.45	5.35	2.14
as $\text{Hg}(\text{NO}_3)_2\text{Aq}$	0.1	5.0	19.8	9.2	10.6	2.12
as HgCl_2Aq	0.4	20.0	50.0	6.95	43.05	2.15
as HgCl_2Aq + excess						
NaOH.....	0.4	20.0	50.0	7.3	42.7	2.13
Nickel—as NiSO_4Aq	0.0396	6.77	39.6	15.7	23.9	3.53
as NiSO_4Aq	0.0396	6.77	39.6	15.45	24.05	3.55
as NiSO_4Aq	0.0198	3.78	19.8	7.85	11.95	3.53
as NiSO_4 + excess NaOH	0.0198	3.78	19.8	7.85	11.95	3.53
Cobalt—as CoCl_2Aq	0.105	17.86	99.0	14.4	84.6	4.73
as CoCl_2Aq , titrated						
after one hour.....	0.0315	5.36	40.0	14.0	26.0	4.85
as CoCl_2Aq , titrated im-						
mediately.....	0.0315	5.36	40.0	15.3	24.7	4.61
as CoCl_2Aq , titrated im-						
mediately.....	0.042	7.15	40.0	7.4	32.6	4.56
as CoCl_2Aq + 0.5 gram						
NaOH, titrated im-						
mediately.....	0.042	7.15	40.0	7.6	32.4	4.52
as CoCl_2Aq + 0.32 gram						
NaOH, titrated after						
five hours.....	0.042	7.15	50.0	16.6	33.4	4.67
as CoCl_2Aq + 0.16 gram						
NaOH, titrated after						
five hours.....	0.042	7.15	50.0	16.7	33.3	4.66
as CoCl_2Aq + ten cc.						
ammonia, titrated						
after five hours....	0.042	7.15	50.0	16.75	33.25	4.65

Metal.	Gram metal added.	Atoms metal added.	Equivalents KCy taken.	Equivalents Cy found by titration.	Difference(=equivalents of Cy combined).	Equivalents Cy combined per atom of metal.
Cobalt—as CoCl_2 Aq alone, titrated after five hours..	0.042	7.15	50.0	16.5	33.5	4.68
Platinum—as H_2PtCl_6	0.06	3.1	19.8	19.4	0.4	0.13
as H_2PtCl_6	0.125	6.4	39.4	38.6	0.8	0.125
as H_2PtCl_6 + excess NaOH.....	0.12	6.2	19.8	19.2	0.6	0.10
Silver—as nitrate (standard)..	2.0
as AgCl.....	0.06475	6.0	20.1	8.1	12.0	2.0
as AgCl.....	0.06475	6.0	20.1	8.05	11.95	1.992
as AgI.....	0.06475	6.0	20.1	8.15	12.05	2.008
as AgI.....	0.06475	6.0	20.1	8.1	12.0	2.0
as AgBr.....	0.05385	5.0	20.1	10.1	10.0	2.0
as Ag_2S dissolved in HNO_3	0.05385	5.0	20.1	10.2	9.9	1.98
Manganese—as $\text{MnCl}_2 + \text{NH}_4\text{Cl}$	0.0242	4.39	19.9	17.0	2.9	0.66
as $\text{MnCl}_2 + \text{NH}_4\text{Cl}$	0.0122	2.2	19.9	18.25	1.65	0.75
as $\text{MnCl}_2 + \text{NH}_4\text{Cl}$	0.0122	2.2	19.9	18.7	1.2	0.55
Copper—series 10	about	3.43
—with excess ammonia.	approaches	3.0
Zinc—series 9	under	4.0
—with excess NaOH.....	approaches	0.0
Cadmium—series 11, varies	0.5
—with excess ammonia	approaches	0.0

Upon standing the final precipitates of silver iodide increased greatly in presence of cobalt, manganese, platinum, and auric compounds: with zinc and copper the tendency was in the reverse direction.

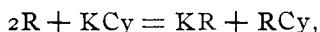
SERIES 13.—EFFECTS OF OXIDIZING AGENTS.

Set I.—These oxidizing solutions were standardized immediately before use by standard thiosulphate, or permanganate, or by both methods. Measured volumes were then added to ten cc. lots of fifth-normal potassium cyanide solution, which were then titrated with twentieth-normal silver nitrate, using three to five cc. ammonia and one-tenth gram potassium iodide as indicator.

Oxidizing agent.	Gram added.	Atoms added.	Equivalents of KCy taken.	Equivalents of Cy found by titration.	Difference(=equivalents of Cy oxidized).	Equivalents of Cy oxidized by one atom.
Iodine (dissolved in KI).	0.051	4.0	19.8	18.0	1.8	0.448
" " " "	0.102	8.0	19.8	15.95	3.85	0.479
" " " "	0.204	16.0	19.8	12.05	7.75	0.482
" " " "	0.306	24.0	19.8	7.95	11.85	0.49
" " " " in KOH	0.255	20.0	9.95	0.3	9.65	0.481
" " " " in KOH	0.356	27.2	20.0	9.1	10.9	0.40
Bromine (water solution)	0.039	4.9	19.8	17.5	2.3	0.47
" " " "	0.196	24.5	19.8	7.75	12.05	0.493
" " " + KOH	0.196	24.5	19.8	8.4	11.4	0.465
Chlorine (water solution)	0.0275	7.8	19.8	16.05	3.75	0.481
" " " "	0.055	15.6	19.8	12.2	7.6	0.488
Chlorine (active chlorine in bleaching powder).	0.0542	15.3	19.8	12.4	7.4	0.483
Chlorine (active chlorine in bleaching powder).	0.1085	30.6	19.8	4.95	14.85	0.484
Oxygen (available oxygen in twenty cc. hydrogen peroxide).....	6.5	19.8	19.7	0.1	0.015
Oxygen (available oxygen in seventy-five cc. hydrogen peroxide).....	24.3	19.8	19.4	0.3	0.012
Oxygen (available oxygen in 0.11 gram sodium peroxide).....	4.7	19.8	19.8	0.0	0.0
Oxygen (available oxygen in 0.38 gram sodium peroxide left two hours)	15.7	19.8	19.7	0.1	0.06
Oxygen (available oxygen in fifty cc. saturated solution of barium peroxide)	1.55	19.8	19.8	0.0	0.0
Oxygen (available oxygen in 100 cc saturated solution of barium peroxide)	3.1	19.8	{ 19.8 to 19.85	{ 0.0 to 0.05	{ 0.0 to 0.016

In the case of iodine, bromine, and chlorine (whether free or in bleaching powder), the proportion of cyanide oxidized evi-

dently approaches that corresponding to the well known equation :



and more closely as the proportion of halogen to cyanogen increases. The variation from five-tenths in the values in the last column may be due to the action of the ammonia added as indicator. The active chlorine in the bleaching powder was determined from the iodine it liberated from potassium iodide in presence of free hydrochloric acid ; in neutral solutions it only liberated about one-twelfth as much iodine ; but its effect on cyanide in alkaline solution corresponds to the full value of the chlorine set free by acid.

The slight effect of potassium nitrate, and of dichromate, on long standing (see series 8), may be due to oxidation ; potassium chlorate was without observable effect.

Permanganates.

Set II.—A number of experiments were made with permanganates, to ascertain the extent to which they oxidized cyanide. The first effect of adding potassium permanganate is to turn the cyanide solution blue, then green and brown, a precipitate (manganese dioxide) falling. The precipitated oxide made it difficult to observe the end of titration ; this was remedied to some extent by adding ammonium chloride. The results varied irregularly with time.

The following tests were made with ten cc. tenth-normal potassium cyanide solution, cyanogen being determined after addition of small amounts of 0.0925 normal potassium permanganate solution.

	(a)	(b)	(c)	(d)
Potassium permanganate added—cc.....	0.0	4.0	4.0	10.0
“ “ “ gram....	0.0	0.01168	0.01168	0.0292
“ “ “ molecule	0.0	0.74	0.74	1.85
Atoms oxygen liberated if reduced to MnO	0.0	1.85	1.85	4.63
“ “ “ “ “ to MnO ₂	0.0	1.11	1.11	2.77
Time of contact before titration—minutes . . .	15.0	30.0	30.0	30.0
Equivalents cyanogen found by titration..	19.8	18.9	18.55	15.8
Difference from (a) = equivalents Cy oxidized.....	0.0	0.9	1.35	4.0

With larger additions of permanganate it was impossible to observe the end-reaction.

From the results shown in series 12 and 13 it is evident that there is a close approximation to constancy in the number of equivalents of cyanogen combined or oxidized by each atom or molecule of some of the interferents. Evidently also, if the conditions can be so adjusted as to secure absolute constancy in the amount of cyanide combined or decomposed by a unit of interferent, a method is obtained for the volumetric estimation of this interferent by titrating with silver nitrate two equal quantities of potassium cyanide, to one of which the interferent has been added. Such is the basis of Denigès' method of estimating silver. The improved method for nickel, published by Thomas Moore,¹ is an application of the same principle.

SERIES 14.—EFFECT OF THIOSULPHATES.

Previous experiments had shown, as had been expected, that the addition of a thiosulphate increased the amount of silver nitrate required in a given estimation. In the following series of tests potassium cyanide solution was treated with various quantities of sodium thiosulphate, and then cyanogen was estimated by tenth-normal silver nitrate, using five cc. ammonia and one-tenth gram potassium iodide as indicator.

The sodium thiosulphate solution used in I and II contained 0.0415 gram of the crystals per cubic centimeter (1 cc. = 1.66 molecules sodium thiosulphate), that used in III and IV 0.01 gram per cc. (1 cc. = 0.4 molecule).

Set I.—Twenty-five cc. fifth-normal potassium cyanide solution titrated with tenth-normal silver nitrate solution.

Sodium thiosulphate added.		Equivalents of cyanogen indicated by titration.	Difference from amount present.	Excess cyanogen for one molecule sodium thiosulphate.	No. of molecules sodium thiosulphate equal in effect to one equivalent cyanogen.
Grams.	Molecules.				
0.0	0.0	49.6	0.0
0.207	8.3	50.8	1.20	0.145	6.91
0.415	16.6	52.12	2.5	0.15	6.64
0.83	33.3	54.4	4.8	0.144	6.91
1.04	41.6	55.8	6.2	0.149	6.71
1.275	50.0	56.8	7.2	0.144	6.95
1.48	58.3	57.6	8.0	0.137	7.30

¹ *Chem. News*, 72, 93.

Set II.—Twenty cc. fifth-normal potassium cyanide solution titrated with tenth-normal silver nitrate solution.

Sodium thiosulphate added.					
Grams.	Molecules.	Equivalents of cyanogen indicated by titration.	Difference from amount present.	Excess cyanogen for one molecule sodium thiosulphate.	No. of molecules sodium thiosulphate equal in effect to one equivalent cyanogen.
0.0	0.0	39.6	0.0
0.415	16.6	41.6	2.0	0.12	8.3
0.830	33.3	43.8	4.2	0.126	7.95
1.245	50.0	45.2	6.6	0.132	7.12
1.660	66.6	48.6	9.0	0.135	7.4
2.075	83.3	51.0	11.4	0.137	7.3

Set III.—Ten cc. fifth-normal potassium cyanide solution titrated with twentieth-normal silver nitrate solution.

0.0	0.5	20.1	0.0
0.125	5.0	20.55	0.45	0.09	11.1
0.25	10.0	20.95	0.85	0.085	11.7
0.375	15.0	21.4	1.30	0.087	11.55
0.5	20.0	21.8	1.70	0.085	11.76
0.75	30.0	22.6	2.50	0.083	12.0
1.0	40.0	23.5	3.45	0.086	11.9

Set IV.—Five cc. fifth-normal potassium cyanide solution titrated with twentieth-normal silver nitrate solution.

0.0	0.0	10.05	0.0
0.125	5.0	10.55	0.5	0.1	10.0
0.25	10.0	10.85	0.8	0.08	12.0
0.375	15.0	11.15	1.1	0.073	13.0
0.5	20.0	11.45	1.4	0.07	14.0
0.75	30.0	12.1	2.05	0.068	15.0
1.0	40.0	13.05	3.0	0.075	13.3

Set V.—In these tests small amounts of potassium cyanide were treated with larger proportions of thiosulphate, and titrated with twentieth-normal silver nitrate, using as indicator one-tenth gram potassium iodide and five cc. ammonia.

	(a.)	(b.)	(c.)	(d.)	(e.)
Sodium thiosulphate added, grams...	0.1	0.415	0.5	1.25	1.25
“ “ “ molecules	4.0	16.6	20.0	50.0	50.0
Equivalents of KCy taken.....	0.0	0.0	2.0	2.0	20.0
Equivalents of cyanogen indicated by titration.....	0.1	0.6	2.8	3.3	22.75

	(a.)	(b.)	(c.)	(d.)	(e.)
Difference = excess of cyanogen indicated	0.1	0.6	0.8	1.3	2.75
No. of equivalents cyanogen equal in effect to one molecule $\text{Na}_2\text{S}_2\text{O}_3$	0.025	0.036	0.04	0.026	0.055
Number of molecules $\text{Na}_2\text{S}_2\text{O}_3$ equal in effect to one equivalent cyanogen..	40.0	27.0	25.0	38.5	18.1

Set VI.—Varying the indicator—potassium iodide—in presence of thiosulphate, using in each case five cc. fifth-normal potassium cyanide solution and three cc. ammonia ; volume fifty cc.

	(a.)	(b.)	(c.)	(d.)
Sodium thiosulphate added, grams....	0	0.25	0.25	0.25
“ “ “ molecules	0	10.0	10.0	10.0
Potassium iodide used, grams	0.1	0.1	0.5	1.0
Equivalents cyanogen indicated by titration	10.05	11.45	11.0	10.75
Error in cyanogen indicated	1.4	0.95	0.7

The end reaction is rendered somewhat indistinct by thiosulphates, and an appreciable error is introduced by 0.01 gram of sodium thiosulphate. For a given amount the actual error in estimating cyanogen increases, the percentage error decreases, with the proportion of cyanide.

The error is far less with the iodide indicator than without it (see series 6, VIII) ; a large increase in the amount of iodide added decreases the error somewhat further. When the proportion of thiosulphate is small, titration gives an excess of about one equivalent of cyanogen for seven molecules sodium thiosulphate (or one milligram for sixty milligrams crystallized sodium thiosulphate). With relatively large amounts of thiosulphate the error introduced per molecule is less, with a large excess about one equivalent cyanogen for thirty-five or forty of thiosulphate.

No satisfactory remedy was found ; various oxidizing agents were tried.

SERIES 15.—EFFECT OF SULPHIDES.

Hydrogen sulphide (a saturated water solution) and alkaline sulphides, were added to potassium cyanide in various proportions : on titrating with silver nitrate by the method of Denigès the dark precipitate of silver sulphide invariably appeared before the end was reached, gradually redissolving at first, but be-

coming permanent before the silver added corresponded to the whole of the cyanogen present, except when the amounts of sulphide were trifling. The device recommended by MacArthur and by Denigès, of precipitating by an alkaline plumbite or its equivalent, was tested and found to work well, except with large proportions of sulphide when slight errors are introduced. It is advisable to use as slight an excess of lead as possible (see effect of lead plumbite, in series 8). It appears to make no difference whether the lead be added as plumbite, or as nitrate following an excess of caustic alkali, provided a sufficient excess of alkali be added. The filtering off of the precipitated lead sulphide is an inconvenience: attempts were made to titrate directly, without filtering off this precipitate, which settles rapidly and affords a good background for observing the end-reaction.

TITRATION IN PRESENCE OF SULPHIDES.

Adding Sodium Plumbite without Filtering off the Lead Sulphide.

Set I.—Using in each case twenty cc. fifth-normal potassium cyanide, titrating with tenth-normal silver nitrate, after addition of five cc. ammonia and one-tenth gram potassium iodide.

Saturated fiftieth-normal hydrogen sulphide				
water added, cc	0	0	10.0	10.0
Lead added (as sodium plumbite + excess				
NaOH) grams	0	0.05	0.05	0.05
Tenth-normal silver nitrate solution re-				
quired, cc.....	19.8	19.7	20.7	20.8
Equivalents of cyanogen indicated.....	39.6	39.4	41.4	41.6

Under these conditions high results were always obtained. Moreover, in presence of the precipitated lead sulphide, the cloud of precipitated silver iodide cleared in about a minute, reappearing on increasing the silver nitrate to 21.7 cc., again clearing and reappearing permanently with 22.1 cc. Hence the apparent amount of cyanogen, found by titrating to a permanent precipitate without filtering off lead sulphide, might be 44.2 equivalents instead of an actual 39.6, an excess of over ten per cent.

Adding Sodium Plumbite and Filtering off the Precipitate Formed.

Set II.—Twenty cc. of fifth-normal potassium cyanide solution were treated with six cc. of hydrogen sulphide water: sodium

plumbite was added, the whole was transferred to a cylinder, shaken well, allowed to settle; twenty cc. of the clear liquid were removed by a pipette and treated as in the previous case.

cc. tenth-normal silver nitrate required: 7.90 (for two-fifths of the whole).

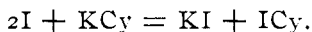
Equivalents of cyanogen indicated: $7.9 \times 2 \times \frac{5}{2} = 39.5$, instead of 39.7.

A similar test at another time gave 44.0 equivalents cyanogen instead of 44.6.

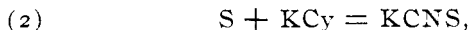
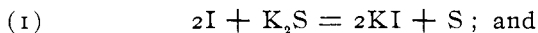
Attempts were made to retain the sulphur in solution as a thio-salt, by the addition of alkaline arsenites, stannates, and antimonites; these all failed, the liquid becoming dark-colored as the amount of uncombined potassium cyanide decreased with the progress of titration; though the actual precipitation of silver sulphide seemed to be preventable. The added salts were themselves found to interfere somewhat.

Various oxidizing agents were experimented with, but all that affected alkaline sulphides appeared to decompose potassium cyanide itself, either directly, or by liberating sulphur, which slowly dissolved with formation of thiocyanate. The halogens readily oxidized sulphides; the peroxides of hydrogen and alkalis were slow and incomplete in action.

A promising method for the removal of sulphide was based on the fact that a weak solution of iodine precipitates sulphur from alkaline sulphides, this redissolving in a minute or two to form thiocyanate. As the direct decomposition of potassium cyanide by iodine under these conditions approximates to the reaction:



and with potassium sulphide and cyanide together:



so that two atoms of iodine in either case decompose one molecule of cyanide, it seemed probable that the interference of small quantities of sulphide could be corrected by adding a constant amount (a slight excess) of a weak iodine solution, and introducing a correction for the amount of added iodine, which correction should be independent of the amount of sulphide oxi-

dized. A number of preliminary experiments confirmed this, subsequent titration with silver nitrate giving, with the correction, quite accurate determinations of the cyanide taken, when the amount of sulphide was small and other reducing agents were absent; with larger proportions of sulphide an appreciable error was introduced, the extent and variation of which were not determined.

Oxidation of the Sulphide by Iodine.

Set III.—Small quantities of a freshly prepared solution of potassium sulphide (fiftieth-normal, so that 1 cc. = 0.00032 gram sulphur) were added to portions of fifth-normal potassium cyanide solution, then a weak solution of iodine in potassium iodide solution (1 cc. = 0.0015 gram iodine) was added to oxidize the sulphide, and cyanogen was estimated as usual.

TO ASCERTAIN THE CORRECTION FOR IODINE ADDED.

	(a)	(b)	(c)	(d)
cc. fifth-normal potassium cyanide taken...	5.0	5.0	10.0	10.0
cc. iodine solution added.....	0.0	30.0	0.0	15.0
cc. twentieth-normal silver nitrate required.	10.05	8.15	20.15	19.2
Correction to be added for iodine.....	1.9	0.95
		for 30 cc.		for 15 cc.

USE OF CORRECTION IN PRESENCE OF SULPHIDES.

	(e)	(f)	(g)	(h)	(k)	(l)	(m)
cc. fifth-normal potassium cyanide solution taken	10.0	10.0	10.0	10.0	10.0	5.0	5.0
cc. fiftieth-normal potassium sulphide solution added	0.5	1.0	2.0	2.0	5.0	0.5	5.0
Milligrams sulphur added as potassium sulphide	0.15	0.32	0.64	0.64	1.6	0.16	1.6
cc. iodine solution used..	15.0	15.0	15.0	15.0	15.0	30.0	30.0
cc. twentieth-normal silver nitrate required to precipitate	19.2	19.2	19.2	19.15	...	8.15	8.35
Correction for iodine.....	0.95	0.95	0.95	0.95	...	1.9	1.9
Equivalents of cyanogen found	20.15	20.15	20.15	20.10	...	10.05	10.25
Error	0.0	0.0	0.0	-0.05	...	0.0	+0.2

In (k) the iodine added was insufficient to oxidize all the sulphide, in (m) an appreciable amount of sulphur separated and did not redissolve, thus introducing an essential error, and also slightly obscuring the end-reaction; this was observed in other

experiments with larger proportions of sulphides; in other experiments with smaller amounts than above no error was observed.

There seems to be no objection to the use of iodine for removing small quantities of sulphide, provided other reducing agents are absent. This avoids the filtration necessitated by the use of alkaline plumbites; when larger proportions of sulphides make it advisable to use lead, it should be added in very slight excess, and a fairly large excess of alkali should be added with it.

ESTIMATION OF CYANOGEN IN ALKALINE CYANIDES: PROCEDURE.

To the solution, in which cyanogen is to be determined, add five cc. commercial ammonia water and two cc. of a five per cent. solution of potassium iodide; titrate in the cold with dilute standard silver nitrate till a faint permanent cloud forms. This is best seen by using a thin flask with a dark back-ground.

This quantity of ammonia is suitable for titrating 25 to 100 cc. of solution; for rapid approximate work, where ten cc. of sample is usually taken, one cc. each of ammonia and iodide solution will be sufficient.

The two indicators may be conveniently combined in one solution. If sufficient ammonia is already present, no more should be added; if a great deal is present a larger addition of iodide (say one gram) will reduce error. Thiosulphates will cause some error, also partially remedied by addition of more iodide.

In presence of *sulphides* in small amount, replace the potassium iodide by five or ten cc. of a solution of about one-half gram iodine and two or three grams potassium iodide in 100 cc. of water, allow to stand five minutes, then add ammonia and titrate. To the result add a correction, which is the difference between parallel tests (i) on some pure dilute potassium cyanide solution, (ii) on an equal amount of potassium cyanide *plus* five or ten cc. of iodine solution.

If the amount of sulphide is large, or if other reducing agents are also present, take twice the usual volume of solution, add some soda, then sodium plumbite in very slight excess, shake well, make up to a definite volume, filter, and use one-half the clear filtrate for titration, rejecting the first few cubic centimeters filtered.

In presence of zinc add a considerable excess of sodium or potassium hydroxide and proceed as above; test the end precipitate with more alkali (if it dissolves add more alkali and continue titration); if insoluble, the cyanogen found represents that contained in potassium zinc cyanide as well as in free potassium cyanide.

The free potassium cyanide can be accurately determined by acidulating another portion of the solution with hydrochloric acid, evaporating till all hydrocyanic acid is expelled, estimating zinc by standard ferrocyanide, and subtracting four equivalents cyanogen or potassium cyanide for each atom of zinc found (or for one milligram zinc subtract one and six-tenths milligram cyanogen or four milligrams potassium cyanide. The free potassium cyanide may be more rapidly and roughly determined by adding first a few drops of a five per cent. solution of potassium ferrocyanide, and titrating directly with silver nitrate until a faint flocculent precipitate forms (using a cc.); then to the same portion adding ammonia, potassium iodide, and soda, and titrating *total cyanogen* (using b cc. altogether). The value a minus a correction indicates cyanogen in free or "available" potassium cyanide: and $(b - a)$ plus the same correction indicates that in double zinc cyanide, the error and correction is increased if free caustic alkali were originally present, and varies slightly with the time occupied in titrating. According to Bettel $a - 0.086(b - a)$ represents the cyanogen "available," and $(b - a) \div 0.921$ gives that in the double cyanide, *if free alkali were originally absent*.

In presence of small amounts of copper the cyanogen combined as double copper cyanide is very approximately calculated by allowing three to four equivalents cyanogen for one atom of copper; the copper being readily estimated colorimetrically by ammonia after expelling hydrocyanic acid with nitric or sulphuric acid.

In presence of calcium, magnesium, or manganese, add ammonium chloride; in presence of aluminum or lead add caustic alkali.

The quantities of gold, silver, and other interfering substances in working solutions are almost always too small to affect the results appreciably; if present in larger proportions, or if bromine or other oxidizers have been added, the amounts of cy-

anogen held by them can be determined approximately from the data in series 12 and 13.

Generally, with impure solutions, the results of titration by this method are more accurate than those obtained by the ordinary Liebig method; with pure solutions the results are practically identical, and in nearly all cases the end-reaction is sharper and an estimation can be more rapidly carried out.

108 grams silver, or 170 grams silver nitrate correspond to 52 grams cyanogen or 130 grams potassium cyanide.

The standard silver solution used may be, with advantage, quite dilute; preferably not over twentieth normal, or one-half per cent. silver.

For technical purposes it is common to take 1.305 grams silver nitrate crystals per 100 cc. of water, when each cc. corresponds to one centigram of potassium cyanide (or four milligrams of cyanogen); or, taking samples of ten cc. each, one cc. of standard silver solution used represents one-tenth of one per cent. potassium cyanide in the liquid tested.

If prepared by dissolving the weighed metal it is not generally necessary to expel all acid. Satisfactory results have also been obtained by using a standard ammoniacal silver solution, made by dissolving pure silver in commercial nitric acid, and adding a slight excess of ammonia.

QUALITATIVE SEPARATIONS WITH SODIUM NITRITE IN ABSENCE OF PHOSPHATES, ETC.¹

BY GILLETTE WYNKOOP.

Received March 8, 1897.

IF a solution of sodium nitrite be added to a solution of ferrous sulphate, the ferrous sulphate solution at first turns a deep brown, and in a short time a greenish brown flocculent precipitate forms, which gradually changes to a fine yellow precipitate, and at the same time a copious evolution of nitrous fumes takes place. If there is a small amount of free acid present in the ferrous sulphate solution, the yellow precipitate occurs almost immediately, and more rapidly still if heated.

A. Peccini and M. Zuco² obtained a precipitate similar to this, but used barium nitrite instead of sodium nitrite. Barium

¹ Read at the meeting of the New York Section, March 5, 1897.

² *J. Chem. Soc.*, 50, 448.