

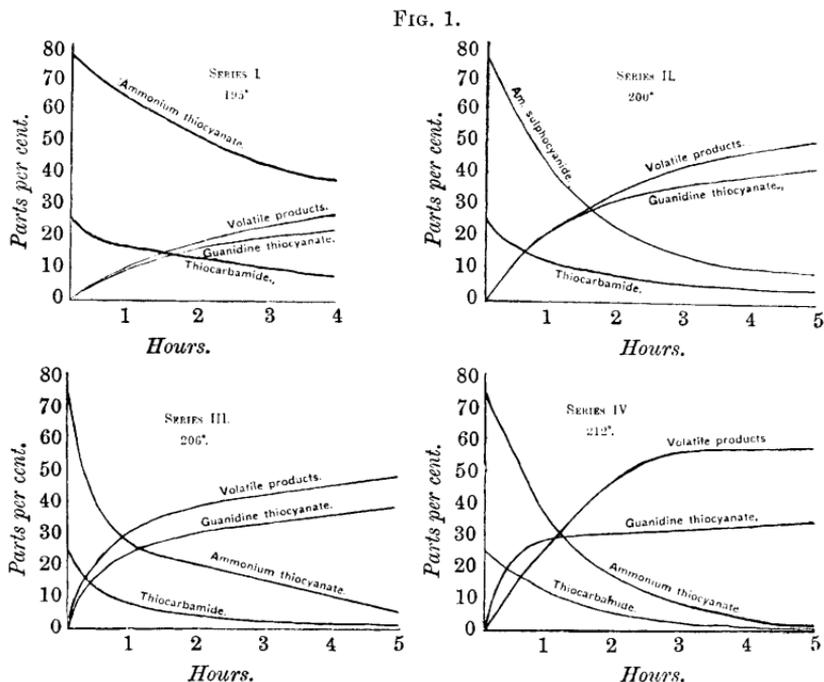
CL.—*Guanidine Thiocyanate: Its Formation from Ammonium Thiocyanate.*

By HANS KRALL.

WHEN either dry ammonium thiocyanate or dry thiocarbamide is heated at 170° equilibrium is attained after forty-five minutes, with the formation of a mixture containing 25 per cent. of thiocarbamide and 75 per cent. of ammonium thiocyanate (Reynolds and Werner, T., 1903, **83**, 1). At this temperature a small quantity of ammonia and hydrogen sulphide is evolved, a trace of non-volatile substance is formed, but no guanidine is produced. If the temperature is raised to 180° , the formation of guanidine thiocyanate begins, with increased evolution of volatile products. The equations put forward by Volhard (*Ber.*, 1874, **7**, 92) to represent the changes that take place are purely hypothetical, and no quantitative experiments appear to have been made with a view to establish the mechanism of the change. The present work was undertaken with that object.

In order to minimise the initial formation of by-products (quite

accidental as regards the change under consideration), it seemed advisable to start all fusions with the pure equilibrium mixture artificially prepared, and consisting of 75 per cent. of ammonium thiocyanate and 25 per cent. of thiocarbamide (Expt. No. I). The use of this mixture as starting point is justified by the results given in table I. Fifteen grams of each substance named were heated in test-tubes side by side in the same bath. It will be seen that



Percentages calculated on the original mixture.

the proportions in the resulting fusion are similar, and that the volatile products are least in the case of the equilibrium mixture.

TABLE I.

One hour at 218°.

Substance heated.	Ammonium thiocyanate.	Thiocarbamide.	Equilibrium mixture.
Volatile	28.0 per cent.	30.4 per cent.	26.6 per cent.
Ammonium thiocyanate	29.6	26.3	30.4
Thiocarbamide	10.4	9.5	11.1
Guanidine thiocyanate	33.0	35.8	35.8
Ratio $\text{NH}_4\text{SCN} : \text{CSN}_2\text{H}_4$	2.84	2.77	2.74

In the experiments II—XIII (Fig. 1), which were carried out in

order to observe the influence of temperature on the course of the reaction, the method adopted was to heat the equilibrium mixture in a series of large test-tubes immersed in an oil-bath. After successive intervals of time a test-tube was removed, the loss by volatilisation determined, and the contents were analysed as described in the experimental part. Owing to the evolution of gas, the temperature of the fusion was always below that of the bath, and was found difficult to regulate, and also a variable quantity of sublimate adhered to the sides of the tube. In these series, therefore, the individual results are only approximate, but they suffice to show clearly the comparative course of the changes. The principal points of interest are:

(1) The changes evidently follow the same general course in each series.

(2) In series I, notwithstanding the low temperature, the volatile products are no less in proportion to the amount of guanidine formed.

(3) In series IV a temperature has been reached at which the volatile products are greatly increased.

In order to establish definitely the fact that the change follows the same course, although more slowly, even below 190°, additional experiments were carefully carried out with similar results (Expt. No. XIV).

In the series No. V (Fig. 2) the procedure adopted was somewhat different. The equilibrium mixture was heated in a beaker suspended in an oil-bath, and samples were removed from time to time. In this case the thermometer could be placed in the fusion, and the method is free from the disadvantages of the former, but the quantity of volatile products cannot be estimated. The results therefore are given as percentages of the fusion, and not of the original mixture.

These curves suggest that the formation of guanidine falls off less rapidly than if the change were unimolecular, and if the velocity-constant is calculated from the equation $K = 1/t \log a/a - x$, where a is the sum of the quantities of ammonium thiocyanate and thiocarbamide, it is found that K increases in value throughout the series, thus:

Time. (in hours).	a .	$1/t \log a/a - x$.
0	87.4	—
1	55.0	0.201
2	30.0	0.233
3	10.5	0.307

Or, if the rate of formation of guanidine is taken from the slope

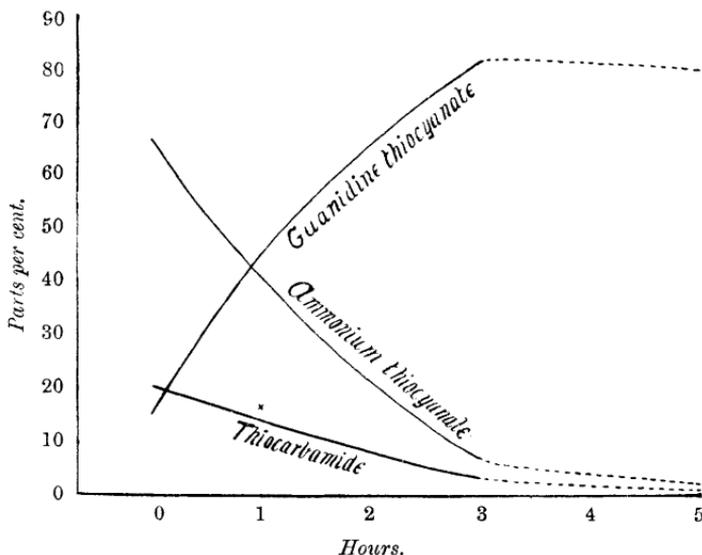
of the curve, and divided by the quantity of reacting substances present, a similar result is obtained :

Time (in hours).	a .	dy/dt .	$1/a \cdot dy/dt$.
1	55	1.69	0.0304
2	30	1.375	0.0458

The slowest change taking place must therefore be one which is influenced by some constant factor, such as the exposed surface, as well as by the concentration.

The volatile products were examined in a separate series of experiments, and invariably consisted of hydrogen sulphide,

FIG. 2.



Percentages calculated on the fusion.

ammonia, carbon disulphide, and thiocyanic acid, or the interaction products of these. The quantity varied not only with the temperature and duration of heating, but with the shape of the vessel used (Expts. Nos. XXVIII and XXIX), but the constituents did not vary throughout the whole of the experiments. The ratio of nitrogen to sulphur is of little value, since guanidine thiocyanate itself evolves ammonia when heated (Expts. Nos. XXII and XXIII).

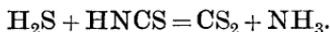
The results obtained have shown that the changes follow the same general course from 170° up to 235°, and probably higher, and it is interesting to note that the equilibrium between thio-

carbamide and ammonium thiocyanate tends to maintain itself as at the lower temperature. The results further suggest that the essential change which comes into play above 170° is the dissociation of thiocarbamide to cyanamide and hydrogen sulphide, the former then uniting with ammonium thiocyanate to produce the corresponding guanidine salt, thus:



The former change agrees with the well-known union of cyanamide with hydrogen sulphide to produce thiocarbamide or with the mercaptans to produce alkyl- ψ -thiocarbamides, and accounts most easily for the large quantities of hydrogen sulphide evolved, whilst cyanamide and ammonium salts are well known to unite very readily to form guanidine salts.

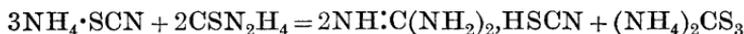
The carbon disulphide is evidently formed by the interaction of thiocyanic (or probably *isothiocyanic*) acid, produced by dissociation, and hydrogen sulphide,* thus:



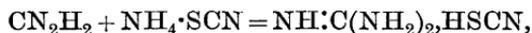
In those experiments in which the volatile products were collected, yellow crystals of ammonium trithiocarbonate were always formed, and the proportions of carbon disulphide, ammonia, and hydrogen sulphide approximated to those required by the equation:



The best single equation, therefore, to represent the whole change is:



The theoretical yield of guanidine cannot be obtained for two reasons. Firstly, owing to mass action, as the amount of guanidine increases, the chance of union of cyanamide and ammonium thiocyanate is diminished, and the very reactive cyanamide forms melamine and other related substances. Secondly, guanidine thiocyanate is not quite stable at the temperatures of experiment, the facts suggesting that the change:

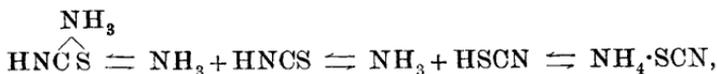


is to some extent reversible. This point is still under investigation (Expts. Nos. XXII, XXIII).

The theoretical view advanced above to account for the production of guanidine depends on the possible dissociation of thiocarbamide to cyanamide and hydrogen sulphide. Now thio-

* This reaction is attributed to Völckel (Beilstein, "Organische Chemie," Vol. I, p. 1272), but no reference is given. The reaction has, however, been verified. (Expt. XXI.)

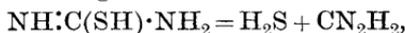
carbamide and ammonium thiocyanate, like their oxygen analogues, undoubtedly owe their interconvertibility to the reversible changes:



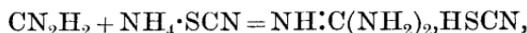
depending on the dissociation of thiocarbamide to ammonia and isothiocyanic acid (see Werner, T., 1912, **101**, 2186). The difficulty of supposing that thiocarbamide dissociates in these two ways simultaneously vanishes if we bear in mind its tautomeric nature, and there is good reason to think that at higher temperatures it tends to change partly into the isomeric form $\text{NH}:\text{C}(\text{SH})\cdot\text{NH}_2$, which obviously ought to lose hydrogen sulphide with ease.

In agreement with this view, it has been found possible to obtain guanidine at lower temperatures by reducing the pressure (Expt. No. XXIV).

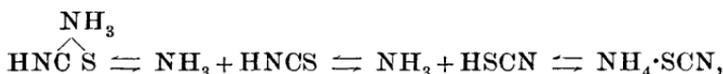
When the equilibrium mixture was heated at 190—200° in sealed tubes, guanidine was formed, and great pressure of hydrogen sulphide was developed, but little ammonia and no carbon disulphide were produced (Expt. XXV). In these conditions it is evident that the changes:



and



proceed, whereas the dissociation:

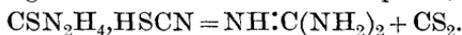


is much retarded, and hence, since little free thiocyanic acid is present, little ammonia and carbon disulphide are formed.

Thus it would seem probable that an even better yield of guanidine than that recorded below (p. 1384) could be obtained by heating in an autoclave, when the reaction might approximate to that represented by the equation:

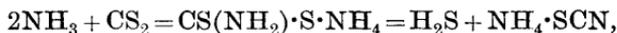


The regular and copious formation of carbon disulphide at all the experimental temperatures suggested at first that it was a primary, rather than a secondary, product of the change, and as an alternative to the explanation given, it is possible that there is transient formation of thiocarbamide thiocyanate, which might decompose into guanidine and carbon disulphide, thus:



A number of attempts to prepare this salt were made, in order to try the action of heat on it, but without success. The weight of evidence, however, is against this scheme, which would leave

the hydrogen sulphide to be accounted for by secondary changes, thus:



whereas the volatile products invariably contain very little thiocyanate, but much hydrogen sulphide. When an intimate mixture of thiocarbamide hydrochloride and potassium thiocyanate was heated, some carbon disulphide was, in fact, formed, but no guanidine could be identified; the disulphide no doubt resulted in this case from a decomposition of isothiocyanic acid (Expts. Nos. XXVI and XXVII).

The sparingly soluble substances formed when the equilibrium mixture is heated are mainly melamine and compounds resembling Claus's so-called thioprussamic acids (*Annalen*, 1875, **179**, 148). These will form the subject of a subsequent communication. They all suggest and confirm the ephemeral presence of free cyanamide during the reaction.

For the preparation of guanidine, the best conditions were found to consist in heating the equilibrium mixture in a narrow-necked flask at 200° for four hours, when a yield of 60 per cent. was obtained.*

No better yield can be obtained at a lower temperature to compensate for the much increased duration of heating, and at higher temperatures the sparingly soluble substances increase considerably. It is better, however, to heat too long, or to too high a temperature, than the reverse, as any unchanged ammonium thiocyanate is difficult to eliminate by recrystallisation without great loss, since ammonium and guanidine thiocyanates have a similar solubility in most solvents.

EXPERIMENTAL.

Expt. No. I.—Preparation of the Equilibrium Mixture.

Dry ammonium thiocyanate † (200 grams) was intimately mixed with the double salt, $\text{NH}_4\text{SCN} \cdot 3\text{CSN}_2\text{H}_4$ (100 grams) (Reynolds and Werner, *loc. cit.*, p. 6). The mixture was gently fused in a porcelain dish, and allowed to cool with continuous stirring until solid. While still warm, the mass was broken up and bottled. It is hygroscopic.

* Ammonium thiocyanate would generally be used instead of the equilibrium mixture; in that case, it is advisable not to raise the temperature too rapidly from 170° to 200°, in order that isomerisation may have time to take place, otherwise the loss by volatilisation is unduly increased.

† This is dried best by heating at 100° (not longer than necessary) and allowing to remain in a desiccator over solid potassium hydroxide, which removes some thiocyanic acid always produced by dissociation.

Method of Analysis.

The following procedure was invariably adopted.

The fusion was allowed to cool, and dissolved in water. If it weighed 10 to 15 grams (Series I—IV) the solution was made up to 500 c.c. When the samples removed were about 5 grams (Series V) the solution was made up to 250 c.c.

Thiocarbamide.—Ten c.c. of the solution were added to 500 c.c. of water; 5 c.c. of dilute sulphuric acid (1 in 8) added, and 4 c.c. of fresh 1 per cent. starch solution; this was titrated with *N*/10-iodine to a full blue colour (Reynolds and Werner, *loc. cit.*).

Ammonia.—Fifty c.c. of solution were boiled briskly for forty-five minutes with 300 c.c. of water and excess of ignited magnesium oxide; the distillate was led into 25 c.c. of *N*-acid, and titrated with *N*-sodium hydroxide, using methyl-orange as indicator. It was found that under these conditions all the ammonia is liberated, whilst the guanidine is not appreciably hydrolysed.

Total Thiocyanate.—Ten c.c. of the solution, with 20 c.c. of water, 5 c.c. of dilute nitric acid (1 in 8), and 25 c.c. of *N*/10-silver nitrate, were shaken in a stoppered bottle; two drops of 10 per cent. iron alum solution were then added, and the whole was titrated with *N*/10-potassium thiocyanate. This method was found better than direct titration with silver nitrate, as it is easier to observe the appearance of the pink colour than its disappearance.

The guanidine thiocyanate was determined by estimating the total thiocyanate, subtracting that due to ammonium thiocyanate, and calculating the difference to the guanidine salt. This method admittedly gives too high a result, especially in the later samples from a fusion, as other thiocyanates are present in small quantity. The error cannot be large, and in no way interferes with the general results. No better way of estimating the guanidine was devised.

Guanidine and Melamine Picrates.

Guanidine picrate crystallises in orange needles, which begin to darken at about 270°, and decompose at 285—290°, with evolution of heat; they explode if heated rapidly. At 12° the solubility is below 7 in 10,000, but in the presence of other salts it appears to be more.

Melamine, which was always formed in our experiments, gives a picrate even less soluble. It separates as a felted mass of canary-yellow needles, which darken at 240°, and become black about 300°.

In simple solution guanidine can be well estimated as picrate,

but the method was useless for our purpose (see Emich, *Monatsh.*, 1891, **12**, 25).

Ethyl Acetate as a Solvent for Guanidine Thiocyanate.

It sometimes becomes necessary to separate mixtures of guanidine and ammonium thiocyanates. The solubilities of both are very similar in water, alcohol, acetone, benzene, chloroform, ether, light petroleum, or carbon disulphide. In ethyl acetate, however, the guanidine salt is not only more soluble, but enters into solution much more readily.

One hundred grams of ethyl acetate dissolve the following quantities, approximately:

Ammonium thiocyanate at the ordinary temperature	3 grams
Thiocarbamide " " "	3 "
Guanidine thiocyanate " " "	20 "
" " near boiling point of solvent.....	40 "

Guanidine thiocyanate, when crystallised from ethyl acetate, drained and washed with a little ether, is obtained colourless and pure.

Expts. II to XIII.—The Influence of Temperature.

The equilibrium mixture in samples of about 15 grams was weighed into large tared test-tubes, which were then plunged into the previously heated oil-bath, so that the required temperature might be attained by the fusion as rapidly as possible. After successive intervals a test-tube was removed, weighed, and the contents were analysed. The results are tabulated below (table II), and shown graphically in Fig. 1.

TABLE II.

Series	I.			II.			III.			IV.		
	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.
Expt. No.												
Temperature of bath	200—204°			210°			218—225°			210—220°		
Estimated temperature of fusion	195°			200°			206°			212°		
Duration (hours)	$\frac{1}{2}$	2	4	1	3	5	1	3	5	1	3	5
Volatile (parts per cent.).....	6.1	18.6	27.0	21.9	42.1	42.1	34.8	42.2	46.7	28.1	56.0	57.0
Ammonium thiocyanate ..	67.6	49.9	36.5	40.3	13.8	9.4	25.6	15.1	5.6	33.9	9.0	[1.5]
Thiocarbamide..	17.8	13.1	7.7	12.5	5.4	4.3	7.5	2.5	1.4	12.1	3.1	[0.5]
Guanidine thiocyanate	5.8	16.6	22.2	22.1	36.3	41.9	27.2	34.1	38.3	29.3	31.3	34.4
Total	97.3	98.2	93.4	96.8	97.6	97.7	95.1	94.0	92.0	103.4	99.4	93.4

Expt. No. XIV.—Equilibrium Mixture Heated Below 190°.

Thirty-four grams were heated in a small retort for two hours, and the volatile products collected. A thermometer in the fusion indicated 188—190°, and the loss of weight was 17·6 per cent. The volatile portion contained all the usual substances (see Expt. No. XX), the free carbon disulphide actually collected being more than 3 per cent. of the original mixture. The fusion contained 19 per cent. of thiocarbamide (15·6 per cent. calculated on the original mixture).

In the preparation of guanidine, therefore, there is no particular point in keeping the temperature below 190°, as usually recommended.

Expts. Nos. XV to XIX.—Velocity of Reaction.

In this series the individual results are more accurate than in the earlier series. The equilibrium mixture was heated in a beaker immersed in an oil-bath, and samples of about five grams were removed, weighed, and analysed. A portion of the later samples was insoluble in cold water, and in such cases the solution was filtered before dilution to a measured volume. The volatile products could not be estimated, and the results are calculated as percentages of the fusion, not of the original mixture. The thermometer was actually in the fusion, and the mean temperature was 205°, varying between 200° and 208°. The first sample was taken when the fusion had attained 205°, and the time was reckoned from then. The results are given in table III, and shown graphically in Fig. 2.

TABLE III.

Series V.—Mean temperature of fusion, 205° (200—208°).
Temperature of bath, 215—230°.

Time (hours)	0	1	2	3	5
NH ₄ ·SCN (per cent.)	66·8	41·1	21·1	7·0	1·7
Thiocarbamide	20·6	16·6 (+)	8·7	3·5	1·0
Guanidine thiocyanate.....	15·0	45·2	65·3	81·7	80·4
Ratio NH ₄ ·SCN : CSN ₂ H ₄ ...	3·24	[2·82] *	2·44	2·01	—

* From curves.

Expt. XX.—Examination of the Volatile Products.

The equilibrium mixture was heated in a flask fitted with an inverted pear still-head, to avoid anything running back into the flask; the evolved vapours were led through a series of wash-bottles containing successively water, dilute acid, and dilute alkali. As soon as all the air had been expelled from the apparatus, the

products were completely absorbed, showing that no nitrogen was evolved. Orange crystals, which proved to be ammonium trithio-carbonate, were formed in the still-head, and carbon disulphide collected in the first wash-bottle, which also contained a trace of thiocyanate. Ammonia and hydrogen sulphide were the only other substances obtained. In various experiments at different temperatures the same products were always found. In one experiment the ratio of nitrogen to sulphur was 1.3N:1.0S (atomic ratio), but as guanidine thiocyanate itself evolves ammonia when heated, such a result is of no value, and the determination was not made in other experiments.

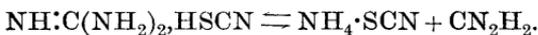
Expt. No. XXI.—Verification of Völckel's Reaction.

A current of hydrogen sulphide, dried with sodium sulphate and phosphorus pentasulphide, was led through a flask containing lead thiocyanate, and thence through a freezing mixture. When the flask was heated on the water-bath, no liquid condensed in the receiver, but when heated to a somewhat higher temperature, carbon disulphide was collected in quantity.

It is obvious that this reaction affords a simple explanation of the formation of carbon disulphide in our experiments.

Expts. Nos. XXII and XXIII.—Action of Heat on Guanidine Thiocyanate.

When this substance is heated it evolves ammonia, and, on treating the fusion with water, is found to be partly insoluble. The solution is alkaline, desulphurises slowly with alkaline solutions of lead, and after acidification decolorises iodine; with sulphuric acid it gives a precipitate of melamine sulphate. These facts suggest that the salt dissociates into cyanamide and ammonium thiocyanate, which would, of course, be partly converted in turn into thiocarbamide; in fact, that the following is a reversible reaction:



When, however, guanidine thiocyanate was heated at 170° in a current of dry hydrogen sulphide, which should combine with the cyanamide, practically no change had taken place after ten hours (titration with iodine in the usual way indicated thiocarbamide = 0.25 per cent.). It is probable that under suitable conditions guanidine thiocyanate would isomerise to guanyl thiocarbamide:



which would desulphurise and decolorise iodine like other substituted thiocarbamides. These changes are under investigation,

but for the purposes of the present communication the two following results suffice to show that, at the temperatures used above, the decomposition, although small, is appreciable.

TABLE IV.

Twenty-five grams of guanidine thiocyanate heated for three hours.

Temperature	180—185°	205—210°
Loss of weight.....	—	2·8 per cent.
Insoluble substances	1·4 per cent.	2·0 ,,
Thiocarbamide indicated by titration with iodine	1·0 ,,	1·4 ,,
Alkalinity in c.c. of <i>N</i> /10-acid...	22·2 c.c.	36·0 c.c.

Expt. No. XXIV.—Equilibrium Mixture Heated under Reduced Pressure.

By reducing the pressure it should be possible to form guanidine at a lower temperature. When the equilibrium mixture was heated at 173° (170—178°) for two hours under a mean pressure of 60 mm., the usual products were evolved, namely, ammonia, hydrogen sulphide, carbon disulphide, and a trace of thiocyanic acid, and the resulting fusion gave the following figures on analysis:

Ammonium thiocyanate.....	61·2 per cent.
Thiocarbamide	22·4 ,,
Guanidine thiocyanate	16·4 ,,
Ratio $\text{NH}_4\cdot\text{SCN} : \text{CSN}_2\text{H}_4$	2·73

Under atmospheric pressure no guanidine is formed at this temperature.

Expt. No. XXV.—Equilibrium Mixture Heated under Increased Pressure.

Five grams were heated in a sealed tube at 190—200° for four hours. A small quantity of sublimate was formed, consisting of ammonium trithiocarbonate. Considerable pressure was developed, and the gas proved to be mainly hydrogen sulphide, with only a trace of ammonia and no free carbon disulphide. The fusion was completely soluble in cold water, and contained no melamine; it contained 11 per cent. of thiocarbamide. The remainder consisted of the thiocyanates of ammonium and guanidine, which were not estimated.

Expt. No. XXVI.—Thiocarbamide Hydrochloride Fused with Potassium Thiocyanate.

It was hoped in this way to obtain the effect of heating thiocarbamide thiocyanate. The mixture was heated at 170° , when hydrogen sulphide and some carbon disulphide were evolved. No guanidine was found in the fusion, and much of the thiocyanic acid had polymerised.

Expt. No. XXVII.—Potassium Thiocyanate Heated in a Current of Dry Hydrogen Chloride.

When heated to 170° , polymerisation took place rapidly, and some carbon disulphide was evolved. This explains the result of the previous experiment.

Expts. XXVIII—XXX.—The Yield of Guanidine Thiocyanate under Different Conditions.

In the following table are given some results which show how the yield is affected by conditions. In these experiments it was found more satisfactory to effect a partial isolation of the products than to analyse the fusion. The method adopted was to treat the fusion with 250 c.c. of warm water, allow to remain overnight, and filter. The filtrate was evaporated as far as possible on the water-bath, and the syrupy residue (which crystallised on cooling) treated with 200 c.c. of absolute alcohol; any substance insoluble in cold alcohol was collected and the filtrate evaporated, first on the water-bath, then in an exhausted desiccator, when guanidine thiocyanate remained.

In these experiments the initial substance was 100 grams of the equilibrium mixture, and the heating was continued at the temperature named for four hours. No. XXVII indicates the best conditions. The mixture was heated in a 150 c.c. round-bottom flask with a narrow neck, immersed to the neck in an oil-bath. In No. XXIX the mixture was heated in an open beaker suspended in the oil-bath, and the temperature was slightly raised. No. XXX is inserted merely for comparison, and shows the effect of a considerably higher temperature, which is evidently to accelerate both the production and decomposition of the guanidine salt. In this experiment a flask was used, and hence the loss by volatile products is again much reduced.

TABLE V.

	XXVIII.	XXIX.	XXX.
Mean temperature of fusion ...	202° (201—204°)	208° (204—209°)	220—230°
Temperature of bath	205—211°	215—222°	
Volatile products	38 per cent.	60 per cent.	37 per cent.
Insoluble in water	trace	4·4 „	16 „
„ alcohol	0·5 „	1·0 „	5 „
Crude guanidine thiocyanate ..	60 „	33 „	40 „

In conclusion, the author desires to express his thanks to Professor E. A. Werner for his invaluable advice and criticism throughout the whole of the work.

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