[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

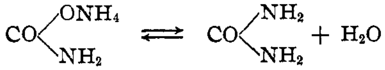
EQUILIBRIA IN THE AMMONIUM CARBAMATE–UREA–WATER–AMMONIA SYSTEM

BY H. J. KRASE[1] AND V. L. GADDY

RECEIVED APRIL 29, 1930 PUBLISHED AUGUST 5, 1930

The present expansion of synthetic ammonia production in this country has stimulated interest in the production of new nitrogen carriers that can be used for agricultural purposes. In this regard, urea is a most promising compound. It has a high nitrogen content, it is readily hydrolyzed in the soil, and it is easily assimilated by plants. Then too, it is important as a starting point for organic syntheses, and for the production of condensation products of urea and formaldehyde. Undoubtedly as the cost of production of urea is reduced, other uses will be developed.

Historical.—The first synthesis of urea from carbamate was probably accomplished by Bassarow[2] in 1870, by heating ammonium carbamate in sealed glass tubes between 130 and 140°. He pointed out that an equilibrium is established between the carbamate dehydration reaction and the hydrolysis of urea with the water liberated according to the equation[2]



$$CO\begin{matrix}ONH_4\\NH_2\end{matrix} \rightleftharpoons CO\begin{matrix}NH_2\\NH_2\end{matrix} + H_2O$$

Bourgeois[3] later investigated the same reaction using, in addition to ammonium carbamate, the carbonate, the sesquicarbonate and the bicarbonate, heating in each case to 130°. The yields of urea varied from 1.5 to 9.52%.

Fichter and Becker[4] have studied this reaction from the standpoint of the effect of temperature, loading density and added water on the equilibrium. They found that the maximum conversion was reached at a temperature of 135° and also that the conversion increased with the loading density or ratio of the weights of the materials to the total volume of the reaction vessel. Added water caused the conversion to fall off, so that the best conversion was obtained with pure ammonium carbamate.

Further work on the conversion of carbamate was carried out by N. W. Krase and V. L. Gaddy.[5] They concluded that because of the endothermicity of the urea formation reaction, the use of a higher temperature would result in a higher yield; that is, they were unable to find an optimum temperature such as reported by Fichter and Becker. The other findings

---

[1] Present address: Swann Research, Inc., Anniston, Ala.

[2] Bassarow, *J. prakt. Chem.*, [2] **1**, 283 (1870).

[3] Bourgeois, *Bull. soc. chim.*, [3] **7**, 48 (1892); **17**, 474 (1897).

[4] Fichter and Becker, *Ber.*, **44**, 3473 (1911).

[5] N. W. Krase and V. L. Gaddy, *J. Ind. Eng. Chem.*, **14**, 611 (1922).

of Fichter and Becker with regard to the effects of loading density and added water on the equilibrium were, however, in general, substantiated by the later work. N. W. Krase and V. L. Gaddy in reporting the effect of water on the urea conversion gave data which by extrapolation to dry carbamate indicated a conversion to urea at 150° of about 44%. Matignon and Fréjacques[6] in a study of the same problem, found a maximum conversion of 43.3% at 145°. In general, it may be said that the equilibrium in the carbamate dehydration reaction at 150° is of the order of 44% of the ammonia converted to urea. No one, to our knowledge, has been able to show a higher conversion starting with ammonium carbamate alone.

In 1917 Fichter, Steiger and Stanisch[7] reported some work in which they heated ammonium carbamate with ammonia. They concluded that in the absence of water, ammonia exerts a beneficial influence only when moderate amounts are used. With larger amounts of ammonia the conversion to urea was found to be adversely affected. They explained the beneficial effect of a moderate amount of ammonia as being due to the prevention of vaporization of carbamate, which increased the amount of salt in the liquid phase. Obviously, an increase in the loading density would have a similar effect. They concluded that a secondary reaction takes place in the presence of large excess of ammonia resulting in the formation of guanidine. In the following work we have tested some of our urea formed in the presence of as much as 300% excess ammonia and have discovered no guanidine.

The possibility of using dehydrating agents to remove the water formed in the reaction has been considered by Matignon and Fréjacques. They performed experiments using dehydrated magnesium sulfate in the liquid and in the gas phase and using calcium chloride in the gas phase. In all cases a conversion lower than that obtained by heating carbamate alone was obtained, probably because of the reaction with the dehydrating agent. To date no satisfactory dehydrating agent for this reaction has been reported.

Preliminary Experiments

The extent to which water enters into the reverse reaction is illustrated in the following three experiments. They were performed in a lead-lined steel bomb, of approximately 100 cc. capacity, heated in an oil-bath at 150° for three and one-half hours. The customary 40 odd per cent. yield was obtained in Expt. 1, in which carbamate alone was heated. Experiments 2 and 3 were designed to show the effect on the equilibrium if the water formed under normal conditions had been removed from the reaction zone. This was accomplished in Expt. 2 by loading the bomb with carbamate and urea only, and in Expt. 3 by loading with urea and a small

---

[6] Matignon and Fréjacques, *Bull. soc. chim.*, **31**, 307 (1922).

[7] Fichter, Steiger and Stanisch, *Verhand. der Natur. Gesell. Basel*, **28**, 66 (1917).

quantity of water. The quantities used were such that in each case the deficiency of water in the system equaled the amount of water that would have been produced in the normal equilibrium. The results of these experiments are recorded in Table I, the last column of which indicates the percentage of carbamate converted to urea or the percentage of urea left undecomposed. Comparison of Expts. 2 and 3 shows that the ordinary test for an equilibrium condition was fulfilled since the conversion approached from the carbamate side of the reaction was also reached from the urea–water side.

TABLE I[a]

RESULTS OF EXPERIMENTS

Experiment	Charge before heating	Calcd. charge after heating	Conversion to urea, %
		44.6 g. carbamate	
1	78 g. carbamate	25.8 g. urea	43.0
		7.7 g. H_2O	
		78.1 g. total	
2	44.5 g. carbamate	27.9 g. carbamate	
	25.8 g. urea	38.6 g. urea	64.2
	70.3 g. total	3.80 g. H_2O	
		70.3 g. total	
		27.00 g. carbamate	
3	60 g. urea	39.40 g. urea	65.3
	10.3 g. H_2O	3.90 g. H_2O	
	70.3 g. total	70.30 g. total	

[a] These experiments were performed by the late C. D. Garby.

The above experiments prove what might be deduced *a priori* from a consideration of the mass law. In order to obtain such increased yields of urea with carbamate as the starting point, it is necessary to find an efficient dehydrating agent which otherwise does not react with the melt and which can be removed readily after the reaction is complete. Ammonia and carbon dioxide appeared most promising for this purpose, since they could not further react with the carbamate or the urea and could be readily recovered and utilized again.

Apparatus and Method

Two duplicate reaction bombs were made of Rezistal 4, a high chrome-iron alloy which had been found to be fairly resistant to the action of the melt. They were approximately 9 cm. in outside diameter and 17 cm. high, having a cavity approximating 100 cc. in volume. Each was provided with a Geophysical type valve, screwed into the plug which was forced onto a gasketed seat by a heavy annular nut. Loading was accomplished by weighing out the pure dry carbamate or urea, introducing it into the bomb, adding the equivalent amount of water and then screwing down the closing plug carrying the valve. The anhydrous ammonia or the carbon dioxide was then weighed in a steel weighing pipet, the large bomb cooled in an ice-bath and the pipet connected to the valve on the bomb. In a short time all of the liquid ammonia or carbon dioxide had run into the bomb. The two bombs, one loaded with carbamate + ammonia, the other with urea + water + ammonia, were heated to 100° in boiling water, and then placed side by side in the bromobenzene vapor-bath shown in Fig. 1. Heating was continued for twenty-four hours, the bombs were removed and placed in a water-bath maintained at 60°. The valves were then cracked and the ammonia distilled into water, where it was determined by titrating an aliquot part. Following distillation of the excess ammonia the bombs were cooled to 15°, the tops removed and the charges washed out and made up to volume. These solutions were then analyzed by determining the total nitrogen by the Kjeldahl method, the urea by the urease method and the ammonia by the direct titration of an aliquot part.

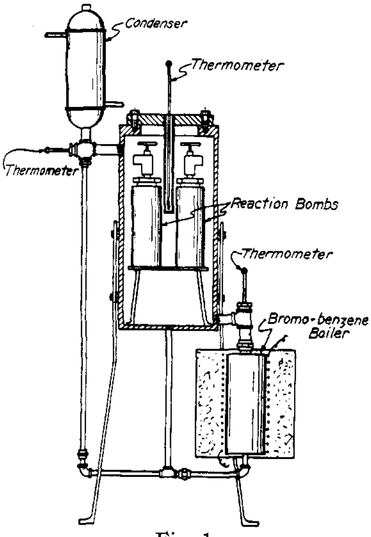


Fig. 1.

Results

The total nitrogen loaded either as carbamate and ammonia or as urea and ammonia varied between 11 and 30 g. in each bomb. The difference between the nitrogen loaded into the bombs at the beginning of an experiment and the nitrogen later found by analysis, was taken as lost and, of course, included errors in weighing and leaks during the run. Probably most of this nitrogen was lost as ammonia from the vapor phase through leaks in the valve and gasket. The actual loss in all of the successful experiments was in the neighborhood of 1 to 7% of the nitrogen loaded. For this reason the calculation of the excess ammonia in each bomb was made on the basis of the total nitrogen as found on analysis and is expressed as percentage of the ammonia loaded as carbamate or as urea, taking into consideration the purity of the salt, which in all cases was in the neighborhood of 99.9% for the urea and 99.4% for the carbamate.

The percentage conversion of the carbamate to urea and the percentage of urea undecomposed by the reverse reaction are expressed as percentage conversion of carbamate ammonia (in Table II) and in the graph of results. These quantities are calculated on the basis of the weights of carbamate or

TABLE II

EXCESS AMMONIA (TEMP., 154–155.6°)

Expt.	Starting materials	Ammonia in excess of carbamate ammonia, %	Conversion of carbamate ammonia to urea, %
1	Carbamate + ammonia	0	43.5
2	Urea + water + ammonia	0	44.0
3	Urea + water + ammonia	19.5	49.7
4	Urea + water + ammonia	23.0	47.7
5	Carbamate + ammonia	23.0	49.5
6	Urea + water + ammonia	23.0	50.2
7	Carbamate + ammonia	23.0	51.5
8	Carbamate + ammonia	26.3	53.0
9	Carbamate + ammonia	45.2	58.2
10	Urea + water + ammonia	45.2	58.7
11	Urea + water + ammonia	53.2	63.5
12	Carbamate + ammonia	63.0	63.5
13	Carbamate + ammonia	76.5	67.0
14	Urea + water + ammonia	82.5	67.0
15	Urea + water + ammonia	89.5	64.0
16	Carbamate + ammonia	96.0	70.5
17	Urea + water + ammonia	173.3	80.2
18	Urea + water + ammonia	210.0	82.5
19	Carbamate + ammonia	222.0	81.5
20	Urea + water + ammonia	279.0	85.2
21	Carbamate + ammonia	280.5	81.0

urea initially loaded into the bomb. The percentage of excess ammonia, based on the ratio of the nitrogen present as ammonia nitrogen to the nitrogen in combination as carbamate and urea is represented by the abscissa in Fig. 2.

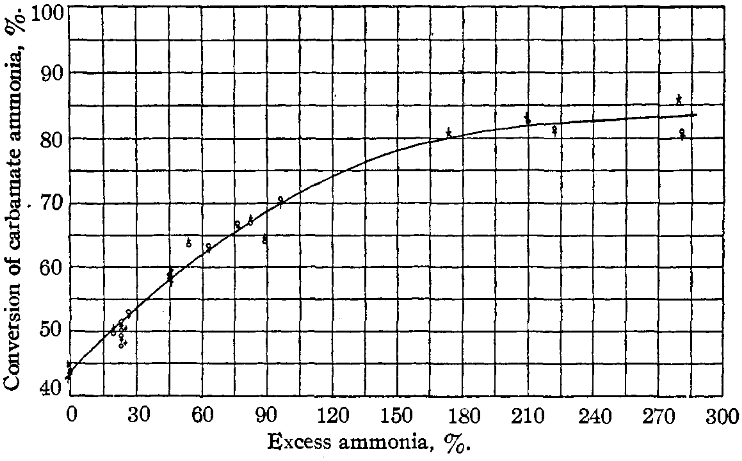


Fig. 2.

Each point on the graph is marked by means of an arrow to indicate whether the equilibrium is approached from the increasing or decreasing urea side of the reaction. The temperature in the experiments varied between 154 and 155.6°.

Excess Carbon Dioxide.—The conversion obtained with no excess ammonia is very close to 44%. This is in agreement with the finding of other investigators as already noted. Several experiments with an excess amount of carbon dioxide were also made. Since they are not shown on the graph they are given in Table III.

TABLE III

EXCESS CARBON DIOXIDE (TEMP., 155.6°)

Expt.	Starting materials	Carbon dioxide, % of combined CO_2 in starting material	Conversion to urea
1C	Carbamate + carbon dioxide	97.0	44.35
2C	Urea + water	100.0	44.0
3C	Carbamate + carbon dioxide	61.2	44.3
4C	Urea + water + carbon dioxide	61.2	45.7

Conclusion

The experimental results show that an excess amount of ammonia over that combined as carbamate acts as a dehydrating agent, removing the water from the active mass, thus preventing its reaction with urea and thereby shifting the equilibrium toward the urea side. Carbon dioxide does not show this effect. The slope of the conversion curve at 300% excess ammonia is such that a complete dehydration is not to be expected with more ammonia, under the conditions here considered.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

THE IODIMETRIC DETERMINATION OF SMALL AMOUNTS OF ZINC

BY H. ARMIN PAGEL AND OLIVER C. AMES

RECEIVED APRIL 29, 1930 PUBLISHED AUGUST 5, 1930

It has been shown by Spacu[1,2] and his co-workers, that zinc can be very accurately determined by precipitating the zinc as zinc pyridine thiocyanate, which may be weighed as such or ignited and weighed as zinc oxide. By employing special apparatus Spacu and Ripan[3] extended their method to the gravimetric determination of as low as 12 mg. of zinc. Unlike most very insoluble zinc compounds, zinc pyridine thiocyanate precipitates in a distinctly crystalline form which transfers and filters perfectly. The precipitate is definite in composition and has the formula,

[1] G. Spacu, *Z. anal. Chem.*, **64**, 338 (1924).

[2] G. Spacu and J. Dick, *ibid.*, **73**, 356 (1928).

[3] G. Spacu and R. Ripan, *ibid.*, **64**, 338 (1924).