

## Biuret Formation in the Manufacture of Urea

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Biuret, if present in urea in high concentrations, has a poisonous effect on plants. For this reason, the mode of formation of biuret in the manufacture of urea has been investigated. The rate at which biuret is produced in molten urea and in concentrated aqueous urea solutions has been measured as a function of ammonia concentration. The relationship thus found can be explained by assuming that the direct conversion of urea into biuret and ammonia plays a secondary part, and that biuret is produced mainly by a reversible reaction between urea and isocyanic acid, the latter being formed from urea with simultaneous evolution of ammonia. The reversible character of this reaction is confirmed by the fact that the amount of biuret in a urea melt may decrease at high ammonia concentrations. Furthermore, the rate of conversion is increased by basic compounds and decreased by acidic compounds.

THE PRINCIPAL IMPURITY in technical urea is biuret, which if present in too large amounts, has a harmful effect on the majority of plants. Most agricultural investigators agree that urea, which is applied in the solid state, may in only very exceptional cases contain more than 2.5% biuret. However, dissolved urea used as a foliar spray causes yellow-tipping in some plant species when the biuret content exceeds 0.5%. Occasionally, 0.25% is mentioned as the maximum allowable limit (1).

Since commercial urea prills very rarely contain less than 1% biuret, foliar sprays are usually prepared from crystalline urea, which contains much less biuret.

In view of the better storage properties of prilled urea, it seemed worth while to investigate the conditions under which the urea process should be carried out to minimize the biuret content. In every stage of manufacturing some biuret is produced, the amount being larger as the temperature is higher and the residence time is longer (2, 4).

Literature data on the conversion of urea into biuret relate mainly to conditions in a nonaqueous medium, such as molten urea. Redemann studied not only the effect of temperature and residence time, but also the influence of the ammonia pressure in the system in which the experiments are performed (2). A patent specification (5) mentions the possibility of converting biuret into urea by treating a biuret-containing melt with ammonia under pressure.

In view of this remarkable effect of ammonia pressure, earlier data on the formation of biuret in which this pressure is not taken into account must be considered of little value. The Central Laboratory of the Dutch State Mines has

done experimental work with the object of collecting new data that might be useful in the manufacture of urea.

Experiments were conducted to determine the rate of biuret formation as a function of urea and biuret concentrations, ammonia concentration (or pressure), and temperature.

### Experimental

**Materials.** The urea used was produced by preparing a substantially saturated solution of technical urea at approximately 70° C., treating this solution with activated charcoal, filtering, and cooling to approximately 35° C. Urea crystallized during the above operations was removed by filtration, washed, and dried at 105° C. It contained less than 0.1% by weight biuret and water.

Biuret was obtained from water-containing biuret supplied by British Drug Houses, Ltd. The biuret was dissolved in water, crystallized, and dried at 105° C. It then contained less than 0.1% by weight cyanuric acid and water. Biuret to be used as an analytical reference was crystallized once more from methanol and dried at 105° C.

**Analytical Methods.** The composition of the solutions and melts obtained was determined by the following analytical methods.

Total nitrogen by the Kjeldahl method. Water content by the Karl Fischer method.

Biuret content, by measuring extinction of light (wave length 550 m $\mu$ ) caused by a copper biuret complex which is produced upon addition of an alkaline solution of potassium sodium tartrate and copper sulphate to the sample (method identical to the I.S.O. specification).

Ammonia in the melt, by direct

titration with acid, using methyl red as an indicator.

Cyanuric acid in the aqueous solution of the sample was precipitated with melamine at pH 4.5 to 5. The precipitate was removed by filtration, dried, and weighed. Cyanuric acid content was calculated from the weight of precipitate.

**Procedure.** The chemical equilibria between urea, biuret, and ammonia and the rates of conversion of urea into biuret (and vice versa) were determined essentially in water-free melts of urea and biuret. In these melts, the temperature of which was adjusted to within 0.1° C., the concentration of ammonia was controlled (and kept constant) by passing gaseous ammonia through it at constant pressures. Change in the concentrations of the urea and biuret was determined analytically on samples collected at different times. From the information thus obtained, the authors could either determine rates of conversion at various ammonia pressures in dependence on the average urea and biuret contents, or ascertain whether chemical equilibrium had established. To find out whether the rate at which ammonia gas was passed through the melt had an effect on the rates of conversion, the gas (1 atm. and 140° C.) was passed at various rates through melts containing little or no biuret. In either case, both during formation of biuret from urea and during conversion of biuret into urea, the rates of conversion at gas velocities between 1 and 500 liters of gas per 100 grams of urea per hour did not show any significant deviations. Although in the formation of biuret from urea, for example, the difference in rate of conversion between duplicate tests performed at high and low gas velocities was approximately 15%, this deviation did not exceed the standard deviation of

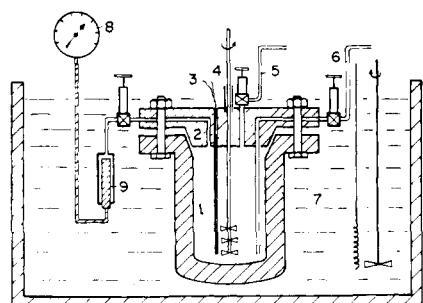


Figure 1. Autoclave in thermostatically controlled oil bath

- |                  |                          |
|------------------|--------------------------|
| (1) Autoclave    | (6) Liquid sampling line |
| (2) Cover        | (7) Oil thermostat       |
| (3) Thermocouple | (8) Manometer            |
| (4) Stirrer      | (9) Teflon diaphragm     |
| (5) Gassing line |                          |

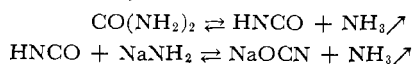
Table I. Rate of Formation of Biuret in a Melt of Urea and Biuret at 140° C. and  $p_{\text{NH}_3} = 1 \text{ Atm.}$

Average Concentration (Moles/Liter)		Velocity of Biuret Formation (Mole/Liter Sec.)
Urea	Biuret	
19.6	0.45	$+0.625 \times 10^{-4}$
17.4	1.70	Small, not measurable
13.2	4.73	$-1.44 \times 10^{-4}$

15% found at constant gas velocity. The relatively large spread in results is due not only to the inaccuracy of the analysis, but also to the heterogeneous character of the reaction medium and the occurrence of consecutive and side reactions, among which the formation of cyanuric acid is the most important. In a urea melt containing 15% by weight biuret, the amount formed at 140° C. and 1 atm. ammonia pressure is as high as 2% by weight per day.

This cyanuric acid formation interferes with the establishment of the chemical equilibrium between urea biuret and ammonia to such an extent that at low ammonia pressures this equilibrium can only be approximated.

At pressures of 1 atm. and lower, determinations were carried out in a glass vessel placed in an oil thermostat. The pressure of ammonia bubbled through the melt was kept constant by means of a pressure controller. The melt was sampled in evacuated sampling vessels placed in liquid nitrogen. In determinations undertaken to determine the effect of acids or bases on reaction velocities, the first sample was collected a few minutes after dissolution of the foreign component. In this way, the measured reaction velocity was prevented from being influenced by reactions between the added compound and the urea, such as:



The equilibria between urea and biuret as well as the reaction velocities at

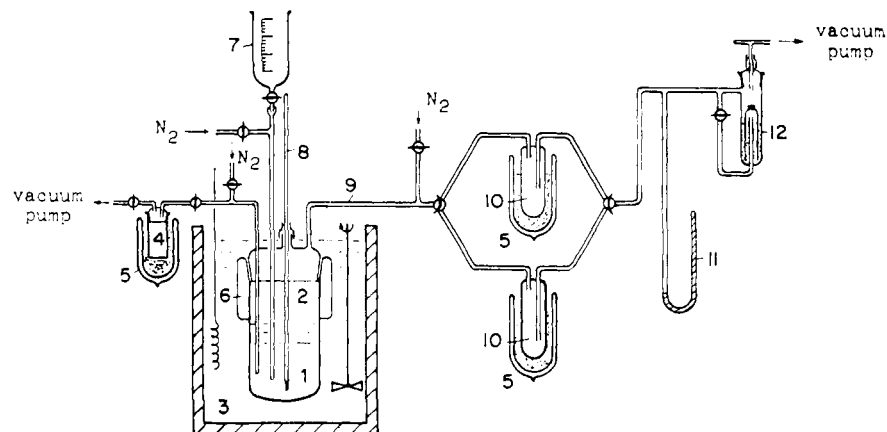


Figure 2. Apparatus for measuring biuret formation in boiling urea solutions

- |                               |                     |                          |
|-------------------------------|---------------------|--------------------------|
| (1) Reaction vessel (300 ml.) | (5) Dewar vessel    | (9) Gas sampling line    |
| (2) Splash plate              | (6) Evacuated shell | (10) Gas sampling vessel |
| (3) Oil thermostat            | (7) Feed vessel     | (11) Hg manometer        |
| (4) Liquid sampling vessel    | (8) Thermometer     | (12) Manostat            |

ammonia pressures above 1 atm. were determined in an autoclave (Figure 1) entirely immersed in an oil-filled thermostat. The melt was brought into close contact with the gaseous phase by means of a stirrer. Liquid samples were collected in a bladder partly filled with water; the gaseous phase was analyzed spectrometrically. In all cases, equilibrium was approached from either side.

The rate of biuret formation in boiling urea solutions was measured with the apparatus shown in Figure 2. In vessel 1, a known amount of concentrated urea solution was boiled at constant rate and under such conditions that the water content remained constant. This was achieved by placing the vessel in an oil bath (+ stirrer) kept at a constant, higher temperature, keeping the pressure over the solution constant and adding water to the solution at such a rate that the temperature of the boiling solution remained constant. The boiling rate was controlled by means of the temperature difference between oil and urea solution and the degree of turbulence of the oil. To prevent drops splashing up against the wall from being heated to a high temperature and unduly accelerating the decomposition, the vapor compartment of the boiling vessel was surrounded by an evacuated glass shell.

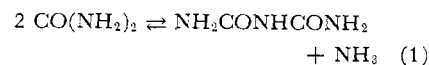
After a steady state had been reached, liquid samples were collected in the liquid sampling vessels at approximately 15-minute intervals, and the evolved gaseous phase was condensed for a given length of time. The rate of biuret formation and the  $p_{\text{NH}_3}$  could be determined by analyzing the liquid and gaseous phases; the boiling rate was calculated from the composition and weight of the gaseous phase condensed.

#### Kinetics of Urea Conversion into Biuret and Vice Versa

In the manufacture of urea from ammonia and carbon dioxide, biuret

forms both in an aqueous solution—e.g., during synthesis—and in a substantially water-free melt—e.g., during evaporation of the resulting solution. Studies on biuret formation have principally been carried out in substantially water-free melts.

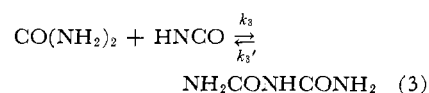
The formation of biuret from urea can, in this case, be represented by the gross reaction equation:



According to this reaction equation, the rate at which biuret is produced should vary with the concentrations of urea and biuret in the reaction medium. This has indeed proved to be so. At 1 atm. ammonia pressure, for example, reaction rates at various biuret contents were determined by analytically measuring the changes in biuret and urea contents as functions of time. The results of these experiments (Table I) show that the rate at which biuret is formed decreases as biuret content of the melt increases.

For a melt containing much biuret,  $d[\text{Bi}]/d\theta$  becomes negative. Therefore, the reaction may proceed in opposite directions depending on the original composition of the melt.

Biuret formation from urea need not be so simple as appears from the gross reaction equation 1. It might also go via the very reactive isocyanic acid, which is produced during the so-called isomerization of urea. In that case, the reaction will proceed as follows:



If the biuret formation goes via reaction 1, then

**Table II. Rate of Formation of Biuret in a Melt of Urea, Biuret, and Ammonia at 140° C. and Various Ammonia Pressures**

pNH <sub>3</sub> (Atm.)	Average Concentrations (Moles per Liter)		Velocity of Biuret Formation (Moles per Liter Sec. × 10 <sup>4</sup> )	Equilibrium Concentration (Moles per Liter)		Reaction Constant	
	Urea	Biuret		Urea	Biuret	( $\frac{1}{\text{Sec.}}$ ) × 10 <sup>4</sup>	Average $\frac{1}{\text{Sec.}}$ × 10 <sup>4</sup>
16.5	12.0	3.80	-3.84	17.3	0.12	1.03	
	14.7	1.99	-1.82	17.3	0.12	0.96	
	14.9	1.76	-1.19	17.3	0.12	0.71	
	15.5	1.37	-1.26	17.3	0.12	0.99	0.91
4.6	12.4	4.73	-2.69	19.0	0.46	0.59	
	14.2	3.45	-2.08	19.0	0.46	0.65	
	16.3	2.20	-0.95	19.0	0.46	0.51	
	19.3	0.210	+0.17	19.0	0.46	0.65	
	19.3	0.114	+0.255	19.0	0.46	0.71	0.62
1.0	13.2	4.73	-1.44 <sup>a</sup>	ca. 17.4	ca. 1.70	0.38	
	19.6	0.45	+0.625 <sup>a</sup>	ca. 17.4	ca. 1.70	0.37	
	19.7	0.41	+0.74 <sup>a</sup>	ca. 17.4	ca. 1.70	0.42	0.39

<sup>a</sup> Average of eight measurements.

**Table III. The Effects of Acids and Bases on the Rate of Formation of Biuret in a Melt of Urea and Biuret**

(Ammonia pressure = 1 atm.)

Catalyst <sup>a</sup>	Average Concentrations (Moles per Liter)		Velocity of Biuret Formation (Moles per Liter Second × 10 <sup>4</sup> )	Approximate Equilibrium Concentration (Moles per Liter)		Reaction Constant	
	Urea	Biuret		Urea	Biuret	$\frac{1}{\text{Sec.}}$ × 10 <sup>4</sup>	Average $\frac{1}{\text{Sec.}}$ × 10 <sup>4</sup>
NH <sub>2</sub> NO <sub>3</sub> (acid)	11.3	5.60	-1.11	16.9	1.65	0.23	
	19.2	0.29	+0.36	16.9	1.65	0.20	0.22
None	13.2	4.73	-1.44	17.4	1.70	0.38	
	19.6	0.45	+0.625	17.4	1.70	0.37	
	19.7	0.41	+0.74	17.4	1.70	0.42	0.39
KOCN (base)	11.7	5.30	-3.11	16.9	1.65	0.69	
	19.2	0.40	+1.30	16.9	1.65	0.75	0.72

<sup>a</sup> Catalyst concentration, 0.5 mole per liter.

$$d[\text{Bi}]/d\theta = k_1[\text{U}]^2 - k_1'[\text{Bi}][\text{NH}_3]$$

$k_1$  = reaction rate constant of forward reaction

$k_1'$  = reaction rate constant of reverse reaction

$[\text{U}]$ ,  $[\text{Bi}]$ ,  $[\text{NH}_3]$  = activities of urea, biuret, and ammonia

$\theta$  = time

For a qualitative explanation of the observed phenomena, activities are replaced by concentrations. Furthermore,

$$\frac{k_1}{k_1'} = K_1$$

where  $K_1$  = equilibrium content.

Hence,

$$d[\text{Bi}]/d\theta = k_1'[\text{NH}_3] \left( \frac{K_1[\text{U}]^2}{[\text{NH}_3]} - [\text{Bi}] \right) \quad (4)$$

If the process goes via reactions 2 and 3, it may be assumed that reaction 2 is in equilibrium. This assumption is based on the difference between the rates of formation of ammonium cyanate from urea and of biuret in urea solutions. The reaction rate constant for the formation of ammonium cyanate in urea solutions with concentrations between

0.005 and 0.1 mole of urea per liter, at 100° C., amounts to  $4 \times 10^{-5}$  liter per second (3). If the same constant is also used for concentrated urea solutions, it can be calculated that the rate at which ammonium cyanate, and also the NH<sub>3</sub> and HCNO in equilibrium with this cyanate, are produced in a solution of 88% by weight of urea ( $\approx 17.7$  moles of urea per liter) and 100° C., amounts to  $4 \times 10^{-5} \times 17.7 = 71 \times 10^{-5}$  moles per liter second. The rate of formation of biuret (2) measured in a saturated urea solution at 100° C. was 0.115% by weight per hour =  $0.37 \times 10^{-5}$  moles per liter second. Since the rate of biuret formation is considerably lower than the rate of HCNO formation, as a first approximation, reaction 2 may be regarded to be in equilibrium.

The rate of biuret formation via reactions 2 and 3 can then be given by

$$d[\text{Bi}]/d\theta = k_3[\text{U}][\text{HCNO}] - k_3'[\text{Bi}]$$

From equation 2, it follows that:

$$[\text{HCNO}] = \frac{K_2[\text{U}]}{[\text{NH}_3]}$$

so that

$$d[\text{Bi}]/d\theta = \frac{k_3 \times K_2 \times [\text{U}]^2}{[\text{NH}_3]} - k_3' \times [\text{Bi}]$$

$$[\text{Bi}] = k_3' \left( \frac{K_2 \times K_1 \times [\text{U}]^2}{[\text{NH}_3]} - [\text{Bi}] \right)$$

When complete equilibrium has been established, then

$$K_1 = \frac{[\text{Bi}]_{\text{eq}} \times [\text{NH}_3]_{\text{eq}}}{[\text{U}]_{\text{eq}}^2}$$

$$K_2 = \frac{[\text{HCNO}]_{\text{eq}} \times [\text{NH}_3]_{\text{eq}}}{[\text{U}]_{\text{eq}}}$$

$$K_3 = \frac{[\text{Bi}]_{\text{eq}}}{[\text{U}]_{\text{eq}} \times [\text{HCNO}]_{\text{eq}}}$$

Hence,

$$K_2 \times K_3 = K_1$$

and consequently

$$d[\text{Bi}]/d\theta = k_3' \left( \frac{K_1[\text{U}]^2}{[\text{NH}_3]} - [\text{Bi}] \right) \quad (5)$$

From equation 4, it follows that the rate at which biuret is formed in a substantially biuret free urea melt ( $[\text{Bi}] \approx 0$ ) does not depend on the ammonia concentration, while equation 5 shows that this rate decreases as the ammonia concentration increases. In practice, the rate of biuret formation in a substantially biuret-free urea melt decreases when the ammonia pressure over the melt increases.

For example, at 140° C. and ammonia pressures of 70 and 760 mm. of Hg, the following values were measured:

Velocity of biuret formation at 70 mm. Hg =  $3.4 \times 10^{-4}$  moles per liter second, at 760 mm. Hg =  $0.9 \times 10^{-4}$  moles per liter second.

As a first approximation, therefore, the conversion seems to be represented by equations 2 and 3. However, these equations do not explain all of the phenomena observed, for this would imply that the above mentioned rates are inversely proportional to the activities of the ammonia in the melt or, by approximation, to the ammonia pressures over the melt. This does not appear to be so; when the ammonia pressure drops to about 1/11 of its original value, the rate of conversion goes up by no more than a factor  $3.4/0.9 = 3.8$ . Hence, the reaction constant must decrease with decreasing ammonia pressure.

The same phenomenon was observed at higher ammonia pressures. Results of measurements at these elevated pressures have been compiled in Table II.

In these tests, the reaction constant was calculated by substituting the value

$$\frac{[\text{Bi}]_{\text{eq}} \times [\text{NH}_3]_{\text{eq}}}{[\text{U}]_{\text{eq}}^2}$$

for  $K_1$  in equation 5. The reaction rate then becomes

$$\frac{d[\text{Bi}]}{d\theta} = k_3' \left( \frac{[\text{Bi}]_{\text{eq}} \times [\text{NH}_3]_{\text{eq}} \times [\text{U}]^2}{[\text{NH}_3] \times [\text{U}]_{\text{eq}}^2} - [\text{Bi}] \right)$$

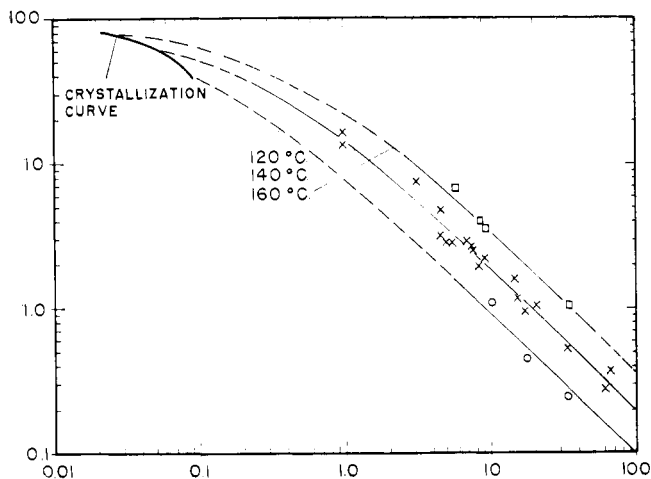


Figure 3. Chemical equilibria between urea, biuret, and ammonia

□ Measurements at 160° C.; ○ measurements at 140° C.; × measurements at 120° C.

For reactions at equal ammonia pressures,  $[\text{NH}_3]_{\text{eq}} = [\text{NH}_3]$ . On the condition that the equilibrium concentrations of urea and biuret corresponding to the existing pressure are substituted, the reaction velocity can be expressed by the following equation:

$$\frac{d[\text{Bi}]}{d\theta} = k_3' \left( \frac{[\text{Bi}]_{\text{eq}} \times [\text{U}]^2}{[\text{U}]_{\text{eq}}^2} - [\text{Bi}] \right)$$

At a given ammonia pressure, the value for the reaction constant calculated by this equation appears to be approximately constant, irrespective of the direction in which the reaction proceeds. It decreases appreciably, however, when ammonia pressure diminishes. The decrease of the reaction constant with  $p_{\text{NH}_3}$  might be explained as follows.

Possibly, biuret is formed, or decomposed, not only via reactions 2 and 3, but also via reaction 1. In that case,  $d[\text{Bi}]/d\theta$  equals the sum of the rates indicated by equations 4 and 5:

$$d[\text{Bi}]/d\theta = (k_3' + k_1' [\text{NH}_3]) \times \left( \frac{K_1[\text{U}]^2}{(\text{NH}_3)} - [\text{Bi}] \right) = k_{\text{over-all}} \left( \frac{K_1[\text{U}]^2}{[\text{NH}_3]} - [\text{Bi}] \right) \quad (6)$$

and the reaction constant  $k_{\text{over-all}}$  increases with  $p_{\text{NH}_3}$ . Upon further examination, however, some striking observations were made, which permit an entirely different explanation. Basic compounds increase the rates of conversion. If a substance acting as proton donor (e.g., an ammonium salt, such as  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$ ) is added to a melt in which the conversion of urea into biuret, or of biuret into urea, proceeds at a definite ammonia pressure (such as, 1 atm.), the rates of conversion will decrease.

If, on the other hand, a base is added

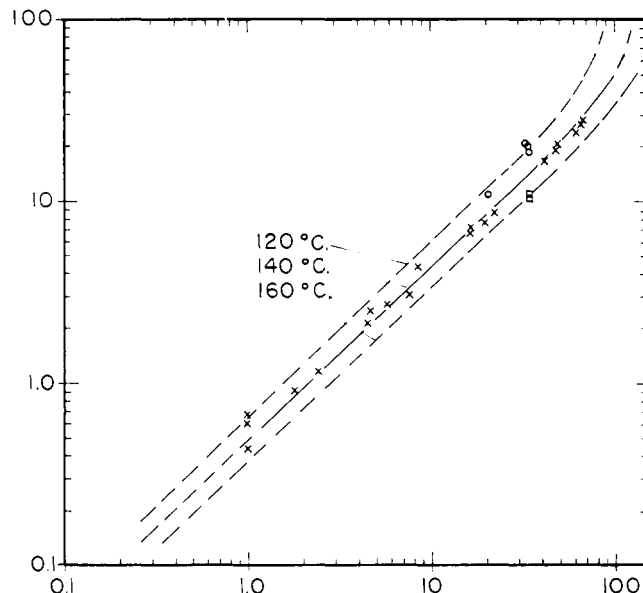


Figure 4. Percentage by weight of ammonia in a melt of urea, biuret, and ammonia at 120°, 140°, and 160° C. (chemical equilibrium)

○ measurements at 120° C.; × measurements at 140° C.; □ measurements at 160° C.

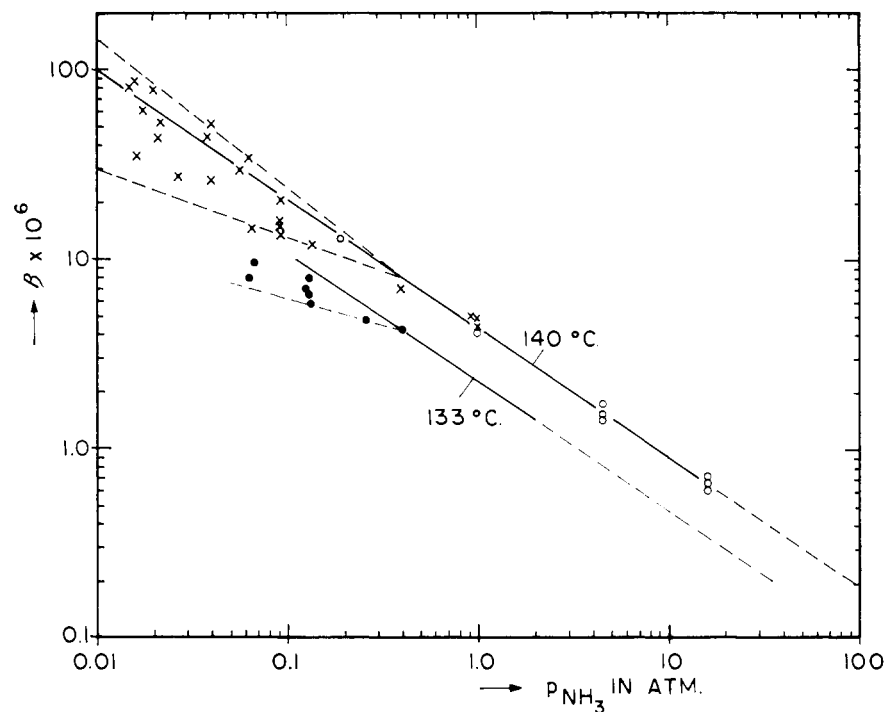


Figure 5. Rate factor for the conversion of urea into biuret (v./v.)

140° C., × conversion of urea into biuret, ○ conversion of biuret into urea; 133° C., ● conversion of urea into biuret

(e.g.,  $\text{KOCN}$ ,  $\text{KOH}$ ,  $\text{NaNH}_2$ ), the rates of conversion go up (Table III). An explanation of this phenomenon may be sought in the catalytic effect of the base, which, to a certain extent, must also be caused by the basic ammonia compound. This might also explain why the reaction constant increases with the ammonia concentration of the melt (increasing  $p_{\text{NH}_3}$ ). In addition to the functions for

the effect of ammonia as the reactant, a second functional relationship for the catalytic effect of this compound must be introduced into equation 5. The latter function, however, cannot be determined separately, so that it is not immediately clear whether the measured deviations from the rate equation derived from reactions 2 and 3 is due to reaction 1 and/or to base catalysis.

**Table IV. Practical Equilibrium Conditions**

Temp. (° C.)	$\frac{U_{eq}^2}{Bi_{eq} \times p_{NH_3}} = \alpha$
120	1050
130	725
140	500
150	350
160	260

**Biuret Formation in Practice**

Equation 6, although in essence indicating the rate of biuret formation, is less suitable for practical calculations of this rate because the high concentrations occurring in the process, in combination with possible catalytic effects, will cause deviations.

These may be compensated for, however, simply by replacing the moles per liter values of the concentrations of urea and biuret by weight percentages, and the ammonia concentration by the ammonia pressure. This causes equation 6 to change to

$$dBi/d\theta = \beta(U^2 - \alpha \times Bi \times p_{NH_3}) \quad (7)$$

$dBi/d\theta$  = grams of biuret per 100 grams (U + Bi) per minute

$\alpha$  =  $U_{eq}^2 / Bi_{eq} \cdot p_{NH_3}$

$\beta$  = factor

U,  $U_{eq}$  = grams of urea per 100 grams (U + Bi)

Bi,  $Bi_{eq}$  = grams of biuret per 100 grams (U + Bi)

$p_{NH_3}$  = ammonia pressure (atm.)

$\alpha$  is a practical indication of the position of the equilibrium, and is analogous to the reciprocal value of  $K_1$  in equation 6. At constant temperature, it proves to have a particular value (Table IV).

This value can be calculated from the equilibrium contents of biuret at ammonia pressures between approximately 1 and 100 atm., found in a number of experiments at 140° C., standard deviation 15%, and in some observations, at 120° and 160° C. (Figure 3). The ammonia contents of these melts are shown in Figure 4. The further influence, if any, of the rate equation by the nonideal properties of the reactants is accounted for in the experimental values of  $\beta$ . In Figure 5, this value is given for some temperatures as a function of the ammonia pressure.

At ammonia pressures considerably below 1 atm., the  $\beta$  values show a large spread. This is caused by the degree to which physical equilibrium has been established between the ammonia content of the melt and the ammonia pressure in the gas phase. The value of  $\beta$  measured during biuret formation under this low pressure proved to be higher, when the mixing between the gas and liquid phases had been more intensive.

As the rate of biuret formation is not appreciably influenced by the presence of small amounts of water, its value in boiling concentrated aqueous urea solutions can be calculated if the ammonia pressure in the vapor phase is known. Unfortunately, the ammonia pressure should be measured first. It would be much simpler if the rate of biuret formation in boiling solutions could be described as a function of directly measurable and controllable variables, such as, temperature, total pressure, and rate at which the water is evaporated from the solution (boiling rate). This is now possible in the following way. From measurements on boiling urea solutions, it has been found that

$$\frac{\Delta Bi}{\Delta \theta} = 0.55 \times W^{0.4} \times P^{-0.35} \times 10^{15.33 - \frac{6058}{T}} \quad (8)$$

where

$\Delta Bi/\Delta \theta$  = grams of Bi per 100 grams of U per minute

T = absolute temperature

W = grams of evaporated water per/100 grams of U per minute

P = total pressure (mm. Hg).

The above equation was derived from experiments at temperatures between 120° and 145° C., pressures between 100 and 760 mm. Hg, and vapor velocities between 0.5 and 5 grams of water per 100 grams of urea per minute. The average deviation between the measured and calculated rates of biuret formation was 10%. The equation is also applicable under conditions outside the measuring range although its accuracy then is slightly less. Allowance must be made, however, for the fact that the vapor velocity should not be higher than approximately 50 grams of water per 100 grams of urea per minute since at velocities exceeding this limit the  $NH_3$  and HCNO formed during the isomerization of urea are expelled so rapidly from the solution that the condition for isomerization equilibrium is no longer satisfied, and equation 8 starts showing large deviations. The amount of biuret formed is then less than the calculated amount. Equation 8 permits calculation of the increase in biuret content in evaporators and vacuum crystallizers, working at not too fast a rate.

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