

## CHEMICAL KINETICS IN THE REACTION BETWEEN NH<sub>3</sub> AND CO<sub>2</sub> UNDER PRESSURE.

By RYO KIYAMA and KEIZO SUZUKI.

The study of the field of kinetics of the reaction between NH<sub>3</sub> and CO<sub>2</sub> under pressure has scarcely been done. Therefore there are many obscure points. In the view of chemical kinetics, this investigation is carried out in order to clear the mechanism of the reaction.

### Apparatus and Procedure.

The schematic layout of the equipment is shown in Fig. 1. A<sub>1</sub> is the reaction vessel made of mild steel, the volume of which is 43 cc; A<sub>2</sub> and A<sub>3</sub>, the bombs, each being filled with liquid NH<sub>3</sub> or liquid CO<sub>2</sub>; A<sub>4</sub>, the spiral tube in order to preheat CO<sub>2</sub> gas; G<sub>1</sub> and G<sub>2</sub>, the burdon type pressure gauges; T<sub>1</sub>, the copper-constantan thermocouple, which is put into the reaction vessel; T<sub>2</sub> and T<sub>3</sub>, the mercury thermometers; the train of points denotes the electric heater; V<sub>1</sub>, ....., V<sub>6</sub>, the valves. The samples, NH<sub>3</sub> and CO<sub>2</sub>, are stored in A<sub>2</sub> or A<sub>3</sub> from each commercial bomb and high pressure is obtained by heating.

The procedure to carry out the experiment at a given ratio of partial pressure of NH<sub>3</sub> and CO<sub>2</sub>

is as follows; gaseous CO<sub>2</sub> is charged into the reaction vessel until the reading of G<sub>1</sub> becomes equal as the partial pressure of NH<sub>3</sub> in the case of experiment and then until the reading of G<sub>1</sub> comes to a definite total pressure of experiment, then the reading of G<sub>2</sub> falls down from P<sub>1</sub> to P<sub>2</sub>. Thus a given quantity of CO<sub>2</sub> is charged into the vessel in use of the reading of P<sub>1</sub> and P<sub>2</sub> in performing the reaction.

The experimental procedure is as follows; gaseous NH<sub>3</sub> is charged into the

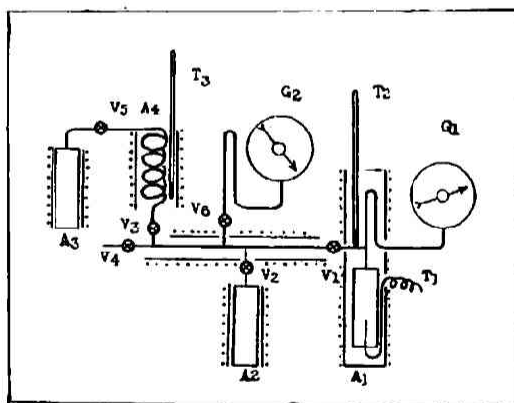


Fig. 1 Schematic layout of equipment.

reaction vessel under a constant pressure and a definite quantity of gaseous  $\text{CO}_2$  is led into the vessel in use of  $\text{G}_2$  as above mentioned. Afterwards the readings of  $G_1$  against time are recorded.

The ratio of packing calculated as  $\text{NH}_4\text{CO}_2\text{NH}_2$  from the pressure is  $0.08 \sim 0.21 \text{ g/cc}$  in the range of the reaction.

Moreover, after the reaction finished, the resultants are cooled rapidly and the gravimetric analysis of urea is carried out.

The reproducibility of the experiment is within 5% of the initial pressure in the readings of  $G_1$ .

### Experimental Results.

The experiments are performed in the range of pressure,  $15 \sim 210 \text{ kg/cm}^2$ , temperature,  $60 \sim 200^\circ\text{C}$ , under various ratios of partial pressure. Fig. 2 ~ Fig. 6 are the pressure change curves plotted from the data of the readings of pressure gauge against time. Fig. 7 is the results of the urea conversion percent curves.

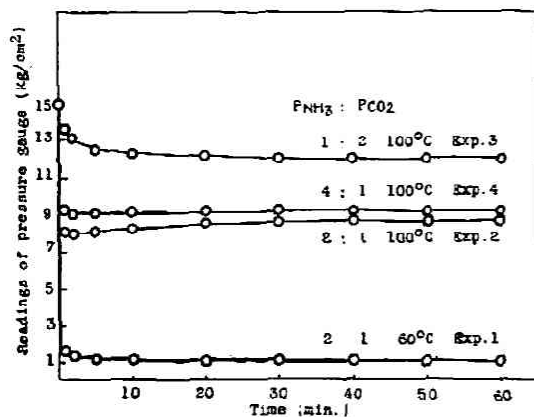


Fig. 2 Pressure change curves.  
Initial pressure  $15 \text{ kg/cm}^2$ .

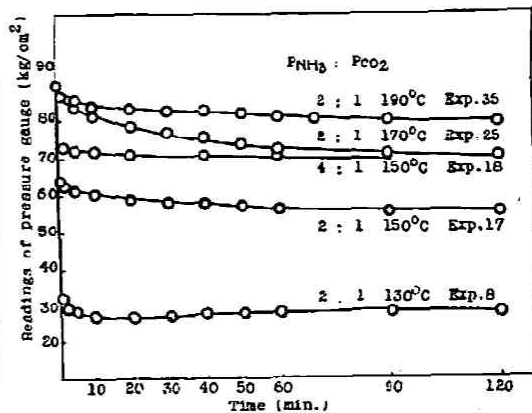


Fig. 3 Pressure change curves.  
Initial pressure  $90 \text{ kg/cm}^2$ .

### Discussions.

From the pressure change curves, there are two cases; one, a rapid pressure decrease occurs, and the other does not, at the initial step of the reaction. Also, it is shown in the urea conversion percent curves, Fig. 7, that there is some difference in the forms of the reaction.

#### (I) The formation of $\text{NH}_4\text{CO}_2\text{NH}_2$ .

From the reason discussed below it can be considered that the rapid pres-

$$\frac{d[\text{NH}_2\text{CONH}_2]}{dt} = k_2[\text{Intermediate product}]. \quad (4)$$

As  $K_1$  is the equilibrium constant, from the step (1)

$$[\text{Intermediate product}] = K_1[\text{NH}_3]^2[\text{CO}_2]. \quad (5)$$

In such a case as  $\text{NH}_4\text{CO}_2\text{NH}_2$  is not formed, accordingly, from Equations (4) and (5) the velocity of urea formation gives

$$\frac{d[\text{NH}_2\text{CONH}_2]}{dt} = K_1 k_2 [\text{NH}_3]^2 [\text{CO}_2] = k [\text{NH}_3]^2 [\text{CO}_2], \quad (6)$$

where

$$k = K_1 k_2. \quad (7)$$

Differentiating with respect to temperature from the Equation (7),

$$\frac{d \ln k}{dT} = \frac{d \ln K_1}{dT} + \frac{d \ln k_2}{dT}. \quad (8)$$

If  $A$  is the activation energy corresponding to  $k$ ,  $A_2$ , the activation energy of step (3), and  $Q_1$ , the heat of reaction in (1), the next relations are given,

$$\frac{d \ln k}{dT} = \frac{A}{RT^2}, \quad \frac{d \ln k_2}{dT} = \frac{A_2}{RT^2}, \quad \frac{d \ln K_1}{dT} = \frac{Q_1}{RT^2}, \quad (9)$$

where it is presumed that the endothermic heat of reaction has a positive sign. From Equations (8) and (9),

$$A = Q_1 + A_2. \quad (10)$$

The heat of reaction in the case of the formation of  $\text{NH}_4\text{CO}_2\text{NH}_2$  from  $\text{NH}_3$  and  $\text{CO}_2$  is about  $-40$  kcal<sup>4)</sup>. Then, it is permitted that the heat of reaction in the step (1) takes the value nearly  $-40$  kcal. The value of  $A$  is about  $-20$  kcal as above described and so  $A_2$  can take a positive value. From these considerations it can be recognized that the velocity constant,  $k$ , of this reaction in which  $\text{NH}_4\text{CO}_2\text{NH}_2$  is not produced has the negative temperature coefficient.

The authors express hearty thanks to the Ministry of Education for the Scientific Research Grant.

*The Laboratory of Physical Chemistry,  
Kyoto University.*

4) K. G. Clark and H. C. Hetherington, *J. Am. Chem. Soc.*, **49**, 1909 (1927)

sure change at the initial time of the reaction is due to the formation of  $\text{NH}_4\text{CO}_2\text{NH}_2$ .

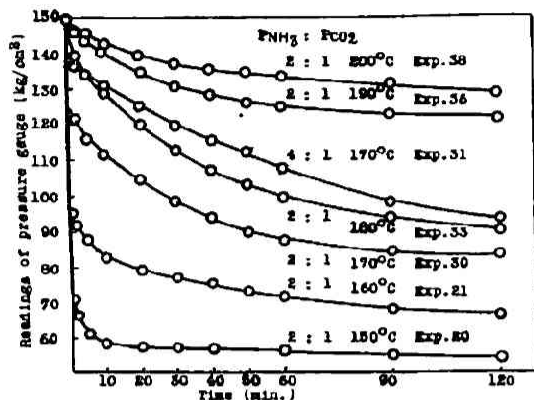


Fig. 4 Pressure change curves.  
Initial pressure 150 kg/cm<sup>2</sup>.

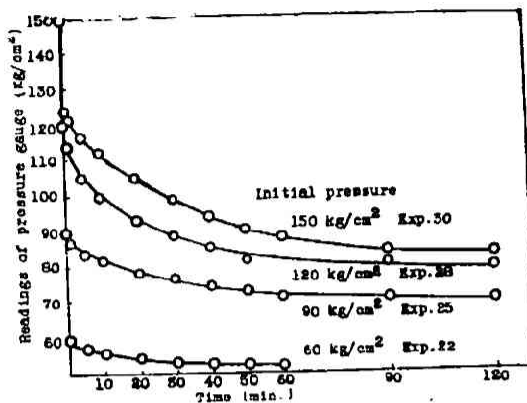


Fig. 5 Pressure change curves.  
 $P_{\text{NH}_3} : P_{\text{CO}_2} = 2 : 1, 170^\circ\text{C}$ .

1) From the dissociation pressure of  $\text{NH}_4\text{CO}_2\text{NH}_2$ .

In the case of Exp. 1 at  $60^\circ\text{C}$  in Fig. 2, the rapid pressure decrease and the heat evolution follow at the initial time, then pressure decreases to 1 kg/cm<sup>2</sup>. The pressure, 1 kg/cm<sup>2</sup>, is the dissociation pressure of  $\text{NH}_4\text{CO}_2\text{NH}_2$  at  $60^\circ\text{C}$ <sup>1)</sup> and under such condition the formation of urea does not occur. Accordingly the curve can be considered as the one of the formation of  $\text{NH}_4\text{CO}_2\text{NH}_2$ .

The comparison between the pressure at the inflexion point\*, where the curve showing the rapid pressure decrease at the initial step crosses the following slow change curve, and the dissociation pressure of  $\text{NH}_4\text{CO}_2\text{NH}_2$  extrapolated from the data of Egan et al<sup>1)</sup>, at the same temperature, is shown in Table I. Both pres-

Table 1

| Exp. No. | Temperature (°C) | Initial press. (kg/cm <sup>2</sup> ) | Press. at the inflexion pt. (kg/cm <sup>2</sup> ) | Dissociation press. of $\text{NH}_4\text{CO}_2\text{NH}_2$ (kg/cm <sup>2</sup> ) |
|----------|------------------|--------------------------------------|---------------------------------------------------|----------------------------------------------------------------------------------|
| 2        | 101 (100)        | 15                                   | 9                                                 | 9                                                                                |
| 8        | 136 (130)        | 90                                   | 36                                                | 37                                                                               |
| 20       | 158 (150)        | 150                                  | 78                                                | 82                                                                               |
| 21       | 165 (160)        | 150                                  | 100                                               | 103                                                                              |
| 30       | 175 (170)        | 150                                  | 133                                               | 141                                                                              |
| 34       | 183 (180)        | 210                                  | 177                                               | 185                                                                              |

( $P_{\text{NH}_3} : P_{\text{CO}_2} = 2 : 1$ )

1) E. P. Egan, J. E. Potts and G. D. Potts, *Ind. Eng. Chem.*, **38**, 454 (1946)

\* In the graphical expression of the equation concerning to the third order velocity constant, described later (Chemical kinetics in the reaction of urea formation), two straight lines cross at the initial time. The crossing point is regarded as the inflexion point.

sures in the comparison nearly coincide. The value shown in the parenthesis in

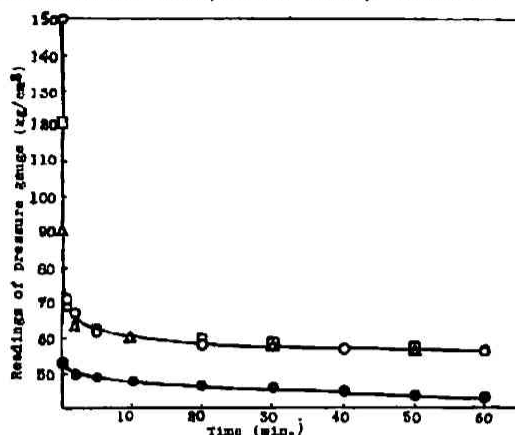


Fig. 6 Pressure change curves, 150°C.

Initial pressure  
 ○ 150 kg/cm<sup>2</sup> Exp. 20  
 □ 120 kg/cm<sup>2</sup> Exp. 19  
 △ 90 kg/cm<sup>2</sup> Exp. 17  
 P<sub>NH<sub>3</sub></sub> : P<sub>CO<sub>2</sub></sub> = 2 : 1  
 ● 53 kg/cm<sup>2</sup> Exp. 15  
 P<sub>NH<sub>3</sub></sub> : P<sub>CO<sub>2</sub></sub> = 3.1 : 1

the temperature column is the temperature before the reaction begins, but owing to the heat evolved at the initial time of the reaction, the temperature rises, and then at the inflexion point it becomes the value shown on the left hand of the temperature column. Fig. 6 shows the rapid pressure decrease at the initial time in every case of the initial pressure except 53 kg/cm<sup>2</sup>, less than the dissociation pressure of NH<sub>4</sub>CO<sub>2</sub>NH<sub>2</sub>, has the inflexion point at nearly the same point.

2) From the relation of the dissociation equilibrium of NH<sub>4</sub>CO<sub>2</sub>NH<sub>2</sub>.

The relation of the dissociation equilibrium of NH<sub>4</sub>CO<sub>2</sub>NH<sub>2</sub> is as follows; NH<sub>4</sub>CO<sub>2</sub>NH<sub>2</sub> (solid)  $\rightleftharpoons$  2NH<sub>3</sub> + CO<sub>2</sub>. In the case of excess of NH<sub>3</sub> or of CO<sub>2</sub>, the next relations are derived from the Mass Law<sup>2)</sup>,

$$\frac{e_1}{\pi} = \frac{2}{3} \left[ \left( \frac{\pi_0}{\pi} \right)^{\frac{1}{2}} - \frac{\pi}{\pi_0} \right], \quad \frac{e_2}{\pi} = \frac{1}{3} \left[ \left( \frac{\pi_0}{\pi} \right)^2 - \frac{\pi}{\pi_0} \right],$$

where  $e_1$ ,  $e_2$  are respectively excess in pressure of NH<sub>3</sub> and of CO<sub>2</sub>,  $\pi_0$  is the normal dissociation pressure of NH<sub>4</sub>CO<sub>2</sub>NH<sub>2</sub> when the ratio of partial pressure of NH<sub>3</sub> and CO<sub>2</sub> is stoichiometric,  $\pi$  is the partial pressure of dissociated NH<sub>4</sub>CO<sub>2</sub>NH<sub>2</sub> in the vapor in the case of having excess in NH<sub>3</sub> or CO<sub>2</sub>. Accordingly, the total pressures are  $e_1 + \pi$  when NH<sub>3</sub> is in excess,  $e_2 + \pi$  in excess of

Table 2

| Exp. No. | Temperature (°C) | Initial press. (kg/cm <sup>2</sup> ) | P <sub>NH<sub>3</sub></sub> : p <sub>CO<sub>2</sub></sub> | Press. (kg/cm <sup>2</sup> ) |       |
|----------|------------------|--------------------------------------|-----------------------------------------------------------|------------------------------|-------|
|          |                  |                                      |                                                           | obs.                         | calc. |
| 4        | 103 (100)        | 15                                   | 4 : 1                                                     | 11.0                         | 11.0  |
| 3        | 103 (100)        | 15                                   | 1 : 2                                                     | 13.8                         | 13.4  |
| 18       | 153 (150)        | 90                                   | 4 : 1                                                     | 73.5                         | 73.9  |
| 31       | 174 (170)        | 150                                  | 4 : 1                                                     | 140                          | 143   |

2) T. R. Briggs and V. Mirdichian, *J. Phys. Chem.*, **28**, 1121 (1924)

$\text{CO}_2$ . It has been experimentally proved that this relation holds in the low pressure region<sup>9</sup>. In Table 2 the comparisons between the observed pressure at the inflexion point and the pressure calculated from the above relation are shown and the consistency in both values is good. The parenthesis in the temperature column denotes the same as in Table 1.

$\text{NH}_4\text{CO}_2\text{NH}_2$  is not formed under the lower pressure than the pressure of dissociated  $\text{NH}_4\text{CO}_2\text{NH}_2$ . When the dissociation pressure is  $150 \text{ kg/cm}^2$ , the temperature is  $176^\circ\text{C}^*$ . From the pressure change curves in Fig. 4, the rapid pressure decrease at the initial time occurs at the temperature below  $170^\circ\text{C}$ , while this rapid change does not above  $180^\circ\text{C}$ . From the correlation between the condition of the  $\text{NH}_4\text{CO}_2\text{NH}_2$  formation and these pressure change curves,  $\text{NH}_4\text{CO}_2\text{NH}_2$  is formed not above  $180^\circ\text{C}$ , but below  $170^\circ\text{C}$ . Also, in Fig. 5,  $\text{NH}_4\text{CO}_2\text{NH}_2$  having the dissociation pressure of  $126 \text{ kg/cm}^2$  at  $170^\circ\text{C}$ , in the case of the initial pressure  $150 \text{ kg/cm}^2$ , the pressure decreases rapidly at the initial time, while in the case of the initial pressure below  $126 \text{ kg/cm}^2$ , the rapid change does not occur. In other cases, the experimental results are satisfactory in consideration.

According to the above consideration, the rapid pressure decrease at the initial time of the reaction is due to the formation of  $\text{NH}_4\text{CO}_2\text{NH}_2$  and the formation of  $\text{NH}_4\text{CO}_2\text{NH}_2$  is dependent upon the initial pressure which is higher than the dissociation pressure of  $\text{NH}_4\text{CO}_2\text{NH}_2$ .

## (II) The formation of urea.

### 1) General consideration.

From the results of the quantitative analysis of urea it may be found that it is always possible to produce urea whether  $\text{NH}_4\text{CO}_2\text{NH}_2$  is formed or not. The urea conversion percent curves, Fig. 7, are the results in the same condition as the pressure change curves in Fig. 4. At  $150^\circ\text{C}$  and  $160^\circ\text{C}$   $\text{NH}_4\text{CO}_2\text{NH}_2$  is formed and at  $180^\circ\text{C}$  and  $190^\circ\text{C}$  is not, as described before. However, the formation of urea occurs in both cases. Accordingly the view that  $\text{NH}_4\text{CO}_2\text{NH}_2$

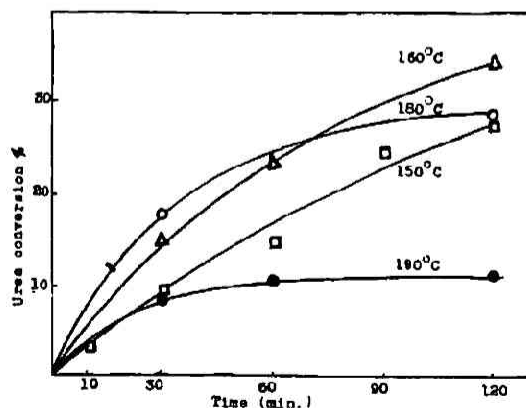


Fig. 7 Urea conversion % curves.  
Initial pressure  $150 \text{ kg/cm}^2$ .  
 $\text{PNH}_3 : \text{PCO}_2 = 2 : 1$

\* cf. 1)

$\text{CO}_2\text{NH}_2$  is the direct intermediate substance in the reaction mechanism is not generally admitted.

In the pressure change curves at the condition that  $\text{NH}_4\text{CO}_2\text{NH}_2$  is not formed (*i. e.* above  $180^\circ\text{C}$  in Fig. 4), the pressure, in any case, decreases below the equilibrium pressure<sup>3)</sup> in the formation of urea. From this result it may be considered that the reaction of urea at this condition goes on in the gaseous state.

In the urea conversion percent curves, Fig. 7, the temperature effect on the urea conversion is reverse between  $160\sim 180^\circ\text{C}$ , namely the limiting temperature of the existence of  $\text{NH}_4\text{CO}_2\text{NH}_2$ .

The effects of pressure and the ratio of partial pressure on the urea conversion percent from the results of analysis are shown in Table 3. Excess of

Table 3

| Exp. No.          | Temperature<br>( $^\circ\text{C}$ ) | Time of reaction<br>(min.) | Initial press.<br>( $\text{kg}/\text{cm}^2$ ) | $\text{P}_{\text{NH}_3} : \text{P}_{\text{CO}_2}$ | Urea conversion<br>(%) |
|-------------------|-------------------------------------|----------------------------|-----------------------------------------------|---------------------------------------------------|------------------------|
| 17 <sub>1</sub> * | 150                                 | 30                         | 90                                            | 2 : 1                                             | 6.0                    |
| 20 <sub>2</sub> * | 150                                 | 30                         | 150                                           | 2 : 1                                             | 9.5                    |
| 35 <sub>1</sub>   | 190                                 | 60                         | 90                                            | 2 : 1                                             | 0.0                    |
| 36 <sub>3</sub>   | 190                                 | 60                         | 150                                           | 2 : 1                                             | 10.6                   |
| 30 *              | 170                                 | 120                        | 150                                           | 2 : 1                                             | 25.9                   |
| 31 *              | 170                                 | 120                        | 150                                           | 4 : 1                                             | 36.3                   |
| 25                | 170                                 | 120                        | 90                                            | 2 : 1                                             | 7.7                    |
| 26                | 170                                 | 120                        | 90                                            | 4 : 1                                             | 11.6                   |

\* The case,  $\text{NH}_4\text{CO}_2\text{NH}_2$  is formed.

$\text{NH}_3$  and the pressure effect upon the yield of urea are recognized whether  $\text{NH}_4\text{CO}_2\text{NH}_2$  is formed or not.

## 2) Chemical kinetics in the reaction of urea formation.

The order of the reaction is obtained from the following relations of the reaction velocities in the two cases 1 and 2.

$$\frac{dx_1}{dt} = k [\text{PNH}_3]_1^m [\text{PCO}_2]_1^n, \quad \frac{dx_2}{dt} = k [\text{PNH}_3]_2^m [\text{PCO}_2]_2^n,$$

when  $[\text{PCO}_2]_1 = [\text{PCO}_2]_2$ ,

$$m = \frac{\log \frac{dx_1}{dt} - \log \frac{dx_2}{dt}}{\log [\text{PNH}_3]_1 - \log [\text{PNH}_3]_2},$$

- 3) M. Tokuoka, *J. Agr. Chem. Soc. Japan*, **10**, 1333 (1934)  
 C. Matignon and M. Fréjacques, *Compt. rend.*, **174**, 455 (1922)  
 R. Kiyama and H. Kinoshita, *This Journal*, **21**, 9 (1951)

CHEMICAL KINETICS IN THE REACTION BETWEEN  $\text{NH}_3$  AND  $\text{CO}_2$ 

29

when  $[\text{PNH}_3]_1 = [\text{PNH}_3]_2$ ,

$$n = \frac{\log \frac{dx_1}{dt} - \log \frac{dx_2}{dt}}{\log [\text{PCO}_2]_1 - \log [\text{PCO}_2]_2},$$

where  $\text{PNH}_3$  and  $\text{PCO}_2$  are the initial partial pressure of  $\text{NH}_3$  and  $\text{CO}_2$  respectively.

Table 4

| Exp. No. | Initial press. (kg/cm <sup>2</sup> ) | $\text{PNH}_3$ | $\text{PCO}_2$ | $m$ | $n$   |
|----------|--------------------------------------|----------------|----------------|-----|-------|
| 23       | 72                                   | 42             | 30             | 1.9 | 1.0 * |
| 25       | 90                                   | 60             | 30             | 2.0 |       |
| 27       | 100                                  | 70             | 30             | 1.8 | 1.0   |
| 22       | 60                                   | 40             | 20             |     |       |
| 24       | 90                                   | 70             | 20             |     |       |

(Temperature, 170°C)

\*  $\text{PNH}_3$ , 42, 40 of Exp. No. 23, 22 are regarded as the same pressure.

Substituting the experimental results in the above relations, the values of  $m$  and  $n$  are obtained, which are shown in Table 4. From the sum of  $m$  and  $n$  the order of the reaction is regarded as the third order. Assuming that  $a$  and  $b$  are respectively the initial partial pressure of  $\text{NH}_3$  and  $\text{CO}_2$  and  $\Delta P$  is the quantity of pressure change, the third order velocity constant is given as follows;

$$k = \frac{1}{a(a-2b)^2} \left\{ \frac{\frac{2\Delta P}{3}(2b-a)}{a\left(a-\frac{2\Delta P}{3}\right)} + 2.303 \log \frac{b\left(a-\frac{2\Delta P}{3}\right)}{a\left(b-\frac{\Delta P}{3}\right)} \right\},$$

but when  $a=2b$ ,

$$k = \frac{9}{8t} \{ (3b - \Delta P)^{-2} - (3b)^{-2} \}.$$

Accordingly, the values of the bracket in the former equation or  $(3b - \Delta P)^{-2}$  in the latter against time are plotted as linear relations and also the tangents are proportional to the velocity constants. The time range satisfied with linearity in the case of  $\text{PNH}_3 : \text{PCO}_2 = 2 : 1$ , is shorter than in the case of  $\text{PNH}_3 : \text{PCO}_2 = 4 : 1$ .

Table 5

| Exp. No. | Temperature (°C) | Initial press. (kg/cm <sup>2</sup> ) | $\text{PNH}_3 : \text{PCO}_2$ | Velocity constant $10^4$ (cm <sup>3</sup> /kg <sup>2</sup> ·min) |
|----------|------------------|--------------------------------------|-------------------------------|------------------------------------------------------------------|
| 25       | 170              | 90                                   | 2 : 1                         | 1.4                                                              |
| 26       | 170              | 90                                   | 4 : 1                         | 1.8                                                              |
| 28       | 170              | 120                                  | 2 : 1                         | 1.6                                                              |
| 33       | 180              | 150                                  | 2 : 1                         | 1.0                                                              |
| 36       | 190              | 150                                  | 2 : 1                         | 0.5                                                              |
| 38       | 200              | 150                                  | 2 : 1                         | 0.3                                                              |

} mean 1.6

It may be considered that the continuation of linearity is due to the opposite reaction that is prevented by excess of  $\text{NH}_3$ . The velocity constants obtained from the above relations are shown in Table 5. That is, the velocity constants have the negative temperature coefficient and the activation energy calculated from the relation of  $\log k - \frac{1}{T}$  is about  $-20$  kcal.

The velocity constants shown in Table 5 are the values obtained when  $\text{NH}_4\text{CO}_2\text{NH}_2$  is not formed. The yields of urea calculated from the velocity constants and the observed yields in the case of the formation of  $\text{NH}_4\text{CO}_2\text{NH}_2$  are shown in Table 6. The calculation is as follows;

Table 6

| Exp. No.        | Temperature (°C) | Velocity constant $10^6$ ( $\text{cm}^4/\text{kg}^2 \cdot \text{min}$ ) | Weight of urea (g) |       |
|-----------------|------------------|-------------------------------------------------------------------------|--------------------|-------|
|                 |                  |                                                                         | calc.              | obs.  |
| 33 <sub>1</sub> | 180              | 1.0                                                                     | —                  | 0.838 |
| 30 <sub>2</sub> | 170              | 1.6                                                                     | 0.8                | 0.720 |
| 21 <sub>1</sub> | 160              | 3.1 *                                                                   | 0.7                | 0.803 |
| 20 <sub>2</sub> | 150              | 4.3 *                                                                   | 0.4                | 0.524 |

(Initial pressure, 150  $\text{kg}/\text{cm}^2$ ;  $P_{\text{NH}_3} : P_{\text{CO}_2} = 2 : 1$ ; time of reaction, 30 min.)

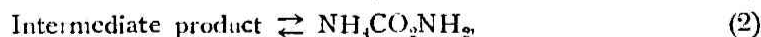
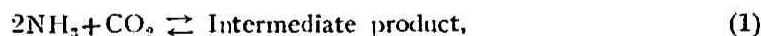
\* extrapolated value.

$$\text{yield of urea (in weight)} \doteq a k \sum_{i=0}^{30} [P_{\text{NH}_3}]^2 [P_{\text{CO}_2}] = a k \sum_{i=0}^{30} \left(\frac{2P}{3}\right)^2 \left(\frac{P}{3}\right),$$

where  $P$  is the reading of pressure gauge,  $a$  is the proportional constant determined by substituting the values at  $180^\circ\text{C}$  ( $\text{NH}_4\text{CO}_2\text{NH}_2$  is not formed) in Table 6. The calculated weight of urea and the observed are the values at 30 minutes. Accordingly, it can be considered that the reaction of urea formation almost proceeds in the gaseous state, even in such a case as  $\text{NH}_4\text{CO}_2\text{NH}_2$  is formed; at least in the initial state of the reaction.

### 3) The reaction mechanism.

From the reason above described the following mechanism is proposed.



The step (2) is possible only when the initial pressure is higher than the dissociation pressure of  $\text{NH}_4\text{CO}_2\text{NH}_2$ . Assuming the equilibrium relation is always established in the steps of (1) and (2) and  $k_3$  is the velocity constant of (3), the velocity of urea formation reduces to