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# Equilibrium of Urea Synthesis. I.

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A test of the equilibrium conversion of $CO_2$ to urea was carried out using a batch autoclave. Some results different from those reported by Frèjacques were obtained, as was expected from the latest data on commercial urea plants. The equilibrium conversion reached its maximum value at about 195°C by 5—15% higher than that reported by Frèjacques. On the contrary, at temperatures above 200°C the value was lower, and falled rapidly with the raise of temperature. This phenomenon may be due to the mechanism of the equilibrium of urea synthesis, and not to the experimental method, as our sampling was made directly from the liquid phase. The equilibrium conversion, $x$, may be expressed with respect to $NH_3/CO_2$, $a$, $H_2O/CO_2$, $b$, and temperature, $t$, as

$$x = \left(0.2616a - 0.01945a^2 + 0.0382ab - 0.1160b - 0.02732a\left(\frac{t}{100}\right) - 0.1030b\left(\frac{t}{100}\right) + 1.640\left(\frac{t}{100}\right) - 0.1394\left(\frac{t}{100}\right)^3 - 1.869\right) \times 100(\%)$$

Therefore, a limited conversion exists in the conventional urea process.

Many investigators have reported the values of actual conversion for commercial reactors by means of the Frèjacques nomograph,[1] and it seemed that the values thus obtained have been taken as the actual conversion in the process (not multiplied by a factor).

Howerver, from the analysis of data obtained with commercial scale reactors, it has become clear that the conversion for the reactor might well be higher than that reported by Frèjacques.

If this is true, the urea process should be improved. In order to confirm this possibility, the static equilibrium conversion should be examined.

For this purpose we measured the equilibrium conversion by an improved method using a batch autoclave, especially with regard to the method of sampling.

The original points of the present report are that, first, the sampling was made directly from the liquid phase and, second, it was made clear that the equilibrium conversion reaches its maximum value at a certain temperature.

The reason why "the direct sampling" must be emphasized is as follows: the popular interpretation of the existence of the maximum conversion depends on the effect of the loading density on the autoclave,[2] because the analyzed value for the equilibrium conversion is based not on the liquid phase, but on the total amount of $NH_4CO_2NH_2$ charged into the autoclave; otherwise, it is thought that a sampling operation might disturb the equilibrium. That is, the higher the temperature becomes in the autocalve at a certain loading density, the less $NH_4CO_2NH_2$ remains in the liquid phase because of the increased amount of $NH_3$ and $CO_2$ transferred into the gas phase. Thus, even though the conversion in the liquid phase increases because of the higher temperature, the amount of urea formed may become less above a certain temperature. Therefore, the (apparent) conversion based on the total amount of $NH_4CO_2NH_2$ charged into the autoclave reaches its maximum value at a certain temperature. Therefore, the larger the loading density is, the higher is the temperature of the maximum conversion.

Therefore, we think that this factor—the loading density—has caused the misunderstanding of the analysis or troubles in many cases. By our improved experimental method, the effect of the loading density can be removed; thus, the consideration of the equilibrium of urea synthesis becomes clearer than before.

In the present paper, our experimental results and a comparison with those of Frèjacques will be mainly described, while in the next paper some theoretical arguments will be presented.

## Conventional Theory

Although urea synthesis has been developed on a large scale since 1950, the basic research on the equilibrium conversion was done long before, and many reports have been published.

The experimental method has been as follows: $NH_4CO_2NH_2$ (solid) is charged into a steel-made bomb or a glass tube, which is then sealed. After the contents had reached the equilibrium state, all of them in the bomb or in the tube were taken out as a sample for analysis; therefore, the eqiuilibrium conversion was calculated on the amount of urea formed relative to the total amount of $NH_4CO_2NH_2$ charged into the bomb or tube. Thus, the conversion was not a real value, but an apparent one.

In this case, the real value was estimated by an extrapolation (from various loading densities) or by a calibration for the gas phase. Even by these unsatisfactory methods, the effects of the excess $NH_3$, the excess water, and the temperature on the equilibrium conversion are rather clear for the most part.

Therefore, besides $NH_3/CO_2$, $H_2O/CO_2$, and the temperature, the parameter of the loading density is neces-

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[1] M. Frèjacques, *Chimie et Industrie*, **60**, No. 1, 22, (1948).

[2] A. Baranski and A. Fulinski, *Chim. Ind. Gen. Chim.*, **99**, No. 11, 1605—1618 (1968).

sary to express the equilibrium conversion. Frèjacques, however, reported that the equilibrium conversion is dependent on $NH_3/CO_2$, $H_2O/CO_2$, and the temperature only as is expressed below:

$$\frac{x(x+b)(1+a+b-x)}{(1-x)(a-2x)^2} = K(t) \tag{1}$$

where $a$: molar ratio of $NH_3/CO_2$ in the total feed,
$b$: molar ratio of $H_2O/CO_2$ in the total feed,
$K$: equilibrium constant dependent on the temperature,
and $x$: conversion of $CO_2$ to urea, expressed in fractions of the total $CO_2$ in the total feed.

The equilibrium constant, $K(t)$, based on a stoichiometric mixture, was assumed also to be valid for a nonstoichiometric mixture; that is,

$$K(t) = \frac{x_{st}^2(3-x_{st})}{4(1-x_{st})^3} \tag{2}$$

where $x_{st}$ is the equilibrium conversion when $a=2$, $b=0$ (for a stoichiometric mixture).
here $K(t)$ is an increasing, monotonous function with respect to the temperature.

Therefore, in most nonstoichiometric cases, the equilibrium conversion has also been supposed to increase as the temperature becomes higher.

Since his publication, no new basic research on the equilibrium conversion has been reported; interpretations have mainly been reported.

The actual conversion in a reactor effluent of an industrial scale was fairly consistent with Eq. (1) within the limits of the accuracy of measurement at that time, so it was thought that the equilibrium conversion obtained by means of Eq. (1) could be adopted for a reactor effluent in all processes.

Although the above description is sufficient for understanding fundamental matters, it will be convenient, in order to facilitate comparison with our results, that more details are given on the Frèjacques theory.

In Eq. (1) the equilibrium conversion is independent of $NH_4CO_2NH_2$, which is an intermediate in this equilibrium system, but, judging from the fact that, under a sufficient pressure, $CO_2$ converts to $NH_4CO_2NH_2$ completely either with excess $NH_3$ or without it, we think that the conversion of $CO_2$ to urea must be determined by the equilibrium between $NH_4CO_2NH_2$ and urea plus water; there is, then, some error in the expression of Eq. (1).

On the other hand, there has been an assumption that excess $NH_3$ decreases the activity of formed water since it promotes the reverse reaction. Next, with regard to the effect of temperature, it has been supposed that the equilibrium conversion increases as the temperature becomes higher unless by-products such as biuret and cyanuric acid (which are condensates of urea after deammoniation) are formed increasingly; however, considering that the temperature of the experiment at that time did not exceed 185°C, we think that the equilibrium conversion at temperatures higher than the above was estimated by extrapolation.

Nevertheless, the above trend seems reasonable, as the urea formation from $NH_4CO_2NH_2$ is an endothermic reaction.

The effect of excess $NH_3$ or water is deduced by a partial differentiation of $x$ with respect to $a$ or $b$ as follows:

$$f(x,a,b) = x(x+b)(1+a+b-x) - K(t)(1-x)(a-2x)^2 = 0$$

$$\frac{\partial x}{\partial a} = -\frac{f_a(x,a,b)}{f_x(x,a,b)}, \quad \frac{\partial x}{\partial b} = -\frac{f_b(x,a,b)}{f_x(x,a,b)} \tag{3}$$

where the temperature is constant.

Under usual conditions, $a$ is about 4.0, $b$ is about 0.5 and the temperature is about 190°C; therefore, $\partial x/\partial a$ is about 0.08[3] and $\partial x/\partial b$ is about 0.16, a value which is not remarkably affected by $b$.

## Experimental

The apparatus used was a batch autoclave with an induction heater which could heat up the contents rapidly, thus making it possible to measure the reaction velocity correctly.

As has been mentioned above, our measurement is characterized by its sampling method; that is, a direct sampling from the liquid phase was made with a rubber bladder.

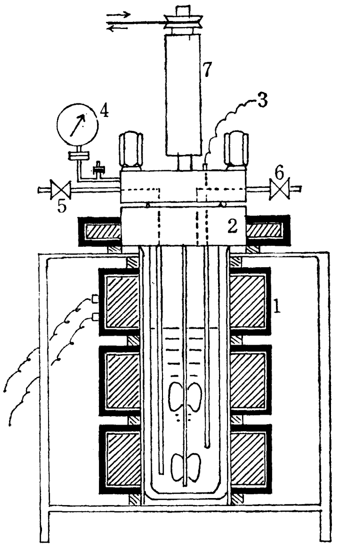

Fig. 1. Batch autoclave.
1: Induction heater, 2: Autoclave (Ti-lined), 3: Thermocouple, 4: Pressure gauge, 5: Sampling valve (liq.), 6: Sampling valve (gas), 7: Agitator

*Apparatus.* The apparatus is composed of the following three units: an autoclave with an agitator, an induction heater, and a temperature controller with its related meters.

*Autoclave*: As is shown in Fig. 1, this is a stainless steel batch autoclave lined with titanium; the inner volume is about 3 liters. All of the parts, such as the cover, the pipes, and the valves, are made of titanium alloy, because stainless steel is much corroded by the urea solution at higher temperatures. The agitator is a rotary type working by magnetic induction.

*Heater and Others*: This heater is composed of four induction coils, as is shown in Fig. 1 tightly fitted to the autoclave. The total output amounts to 35 kW. The temperature of the solution in the autoclave reaches 200°C from room temperature in only 12 min. The input current for heating is controlled with a pulse-type.

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[3] This figure corresponds to the increase in conversion when the excess of $NH_3$ is increased by 50%.

TABLE 1. OBSERVED EQUILIBRIUM CONVERSIONS

| Exp No | Temp.[a] (°C) | Press.[a] ($kg/cm^2G$) | $NH_3/CO_2$[b] (mol/mol) | $H_2O/CO_2$[b] (mol/mol) | Conv. (%) | $R_F$ (%) | Remarks |
|---|---|---|---|---|---|---|---|
| R-63 | 161.5 | 99.0 | 3.95 | 0.13 | 76.1 | 117.3 | Started with carbamate[c] |
| R-62a | 161.5 | 93.0 | 3.88 | 0.43 | 68.8 | 118.09 | |
| R-61 | 161.5 | 83.0 | 4.03 | 1.03 | 61.4 | 123.8 | Started with carbamate |
| R-57 | 161.5 | 92.0 | 4.37 | 0.84 | 67.6 | 122.7 | *ibid.* |
| R-63 | 171.5 | 116.0 | 3.94 | 0.11 | 78.1 | 115.9 | *ibid.* |
| R-58 | 171.5 | 100.0 | 3.89 | 0.85 | 64.9 | 120.8 | *ibid.* |
| R-56 | 171.5 | 111.0 | 4.49 | 0.75 | 69.8 | 116.3 | *ibid.* |
| R-62 | 171.5 | 116.0 | 4.59 | 1.02 | 73.5 | 129.4 | *ibid.* |
| V-11 | 176.5 | 120.0 | 4.01 | 0.09 | 78.6 | 113.2 | |
| V- 8 | 176.5 | 113.0 | 4.06 | 0.53 | 70.8 | 115.0 | |
| V-14 | 176.5 | 108.0 | 4.23 | 0.92 | 67.3 | 118.4 | |
| V-23 | 176.5 | 130.0 | 5.07 | 0.13 | 83.4 | 111.0 | |
| V-33 | 176.5 | 127.0 | 5.02 | 0.56 | 78.1 | 115.3 | |
| V-25 | 176.5 | 118.0 | 5.00 | 0.86 | 74.6 | 118.2 | |
| U-38 | 186.5 | 190.0 | 2.69 | 0.70 | 57.5 | 122.1 | |
| U-11 | 186.5 | 148.0 | 4.00 | 0.06 | 79.2 | 110.0 | |
| U- 7 | 186.5 | 145.0 | 4.04 | 0.28 | 75.4 | 111.0 | |
| U-14 | 186.5 | 135.0 | 4.24 | 0.89 | 68.4 | 114.1 | |
| U-28 | 186.5 | 177.0 | 5.14 | 0.13 | 83.2 | 107.3 | |
| U-24 | 186.5 | 168.0 | 5.12 | 0.48 | 79.7 | 110.8 | |
| U-25 | 186.5 | 155.0 | 4.95 | 0.84 | 74.5 | 113.3 | |
| U-38 | 196.5 | 220.0 | 2.63 | 0.63 | 57.9 | 116.6 | |
| U- 6 | 196.5 | 172.0 | 3.09 | 0.39 | 65.6 | 110.2 | |
| U-12 | 196.5 | 183.0 | 3.93 | 0.07 | 79.5 | 108.3 | |
| U-17 | 196.5 | 182.0 | 4.03 | 0.30 | 76.8 | 109.7 | |
| R-24 | 196.5 | 180.0 | 3.88 | 0.56 | 74.5 | 115.5 | Started with carbamate |
| U-15 | 196.5 | 172.0 | 4.16 | 0.94 | 68.2 | 111.4 | |
| U-29 | 196.5 | 211.0 | 5.16 | 0.13 | 82.7 | 103.9 | |
| R-46 | 196.5 | 210.0 | 5.36 | 0.39 | 80.4 | 104.8 | Started with carbamate |
| R-51 | 196.5 | 198.0 | 5.09 | 0.76 | 76.5 | 108.9 | *ibid.* |
| R-28 | 201.5 | 202.0 | 3.89 | 0.41 | 71.9 | 105.3 | Started from 50% of conversion |
| U- 6 | 206.5 | 232.0 | 3.16 | 0.37 | 66.1 | 105.0 | |
| U-11 | 206.5 | 224.0 | 3.93 | 0.04 | 79.5 | 104.6 | |
| U-19 | 206.5 | 232.0 | 4.13 | 0.54 | 72.0 | 104.0 | |
| U-15 | 206.5 | 225.0 | 4.22 | 0.95 | 67.6 | 105.3 | |
| U-31 | 206.5 | 257.0 | 5.04 | 0.12 | 81.6 | 100.6 | |
| U-34 | 206.5 | 245.0 | 5.04 | 0.58 | 75.8 | 101.5 | |
| R-51 | 206.5 | 248.0 | 5.05 | 0.76 | 74.2 | 102.4 | Started with carbamate |
| U-13 | 216.5 | 297.0 | 4.03 | 0.05 | 77.4 | 98.7 | |
| U- 9 | 216.5 | 315.0 | 4.09 | 0.51 | 66.4 | 92.6 | |
| U-16 | 216.5 | 304.0 | 4.24 | 0.94 | 64.5 | 96.2 | |
| U-32 | 216.5 | 315.0 | 5.00 | 0.10 | 79.3 | 95.5 | |
| R-53 | 216.5 | 324.0 | 5.17 | 0.90 | 65.1 | 88.1 | Started with carbamate |
| U-13 | 226.5 | 378.0 | 4.07 | 0.05 | 72.5 | 90.0 | |
| U-10 | 226.5 | 400.0 | 4.12 | 0.30 | 64.1 | 83.1 | |
| U-16 | 226.5 | 415.0 | 4.21 | 0.91 | 51.8 | 74.3 | |
| U-22 | 226.5 | 413.0 | 5.22 | 0.13 | 71.5 | 83.9 | |
| R-54 | 226.5 | 447.0 | 5.16 | 0.81 | 61.0 | 79.1 | Started with carbamate |

a) Final value reached at the equilibrium state.

b) Molar ratio in a taken sample (equal to that in the liquid phase in the autoclave).

c) $NH_4CO_2NH_2$ was used as the starting material instead of urea plus water.

*Procedure.* For experimental convenience, the charge of materials into the autoclave in most cases was carried out as follows; at first urea plus water (1: 1 molar ratio) was charged in instead of $NH_4CO_2NH_2$; next, excess water, and at last, excess $NH_3$ in the liquid state, was charged in. The total amount charged was about 2.1 kg, which corresponded to about 0.7 g/cc of the so-called loading density. In order to confirm the completion of the equilibrium, $NH_4CO_2NH_2$ was sometimes used as the starting material.

The autoclave was purged of air before the charge of liquid $NH_3$ by light evacuation. After the finish of the charge, heating was started, and then, after a given temperature of the autoclave had been reached, the autoclave was kept at the constant condition for 1—2 hr or longer. Then, after the confirmation of no change in pressure, a sample of liquid (also sometimes one of gas) was directly taken out from the liquid phase in the autoclave (also sometimes from the gas phase) using a weighed rubber bladder with water in it for dilution. About a 15 g sample was taken out and then analyzed by the following methods.

*Analysis.* After the above sampled solution had been diluted in a volumetric flask, each component was determined in aliquots by taking out a portion.

Urea: drying and weighing method

$NH_3$: back titration after the removal of $CO_2$ by excess $H_2SO_4$

$CO_2$: gravimetry as $BaCO_3$,[4] which is precipitated by $Ba(NO_3)_2$

Biuret: colorimetry by the cupric complex salt method.

The amount of pure urea is obtained by the subtraction of the amount of the biuret.

$H_2O$: a residue (assuming that the amount of any other component is negligible.)

In addition to the determinations of the above components, detections for cyanuric acid, melamine, *etc.* are carried out qualitatively if necessary.

## Results

Although some experiments for reaction velocity were carried out, only the results on the equilibrium state will be shown in detail in this paper.

The periods of keeping the solution at a given temperature, was 1—2 hr when the temperature was above 180°C, and about 5 hr when it was below 180°C. The ranges of experimental conditions were as follows:

$NH_3/CO_2$ (mol) ÷ 3—5

$H_2O/CO_2$ (mol) ÷ 0—1.0

Temperature ÷ 170—220°C

The results are shown in Table 1 and in Figs. 2—6. The ratio, $R_F$, of the equilibrium conversion observed to that of Frèjacques is also shown by the percentages in Table 1.

## Discussion

*Experimental Data.* First, the effects of three factors, $NH_3/CO_2$, $H_2O/CO_2$, and temperature, on the equilibrium conversion will be mentioned and compared with those reported by Frèjacques.

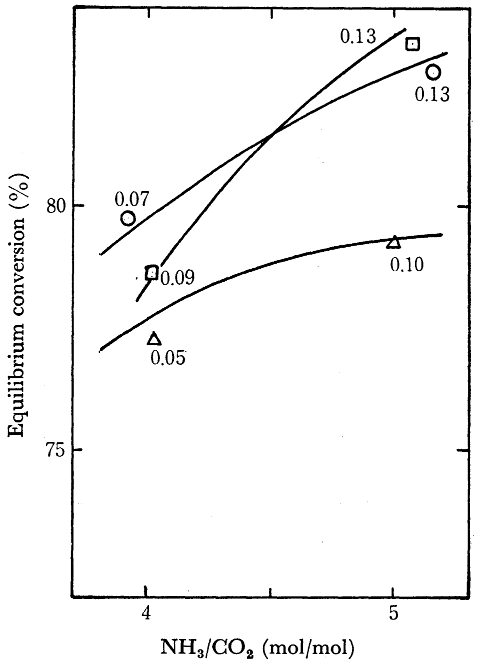

Fig. 2. Effect of $NH_3/CO_2$ on equil. conversion. Each suffix shows $H_2O/CO_2$
-□- 176.5°C, -○- 196.5°C, -△- 216.5°C

*Effect of $NH_3/CO_2$* (*Cf.* Fig. 2): The tendency for the rate of increase to become slower with an increase in the $NH_3/CO_2$ ratio is similar to that reported by Frèjacques. That is, $\partial^2 x/\partial a^2 < 0$, the increase in the equilibrium conversion is 1—1.5% per 0.2 of the increase in $NH_3/CO_2$ (corresponding to a 10% excess of $NH_3$), and at temperatures higher than 200°C the effect of $NH_3/CO_2$ is not so much as that reported by Frèjacques.

*Effect of $H_2O/CO_2$* (*Cf.* Figs. 3, 4): In Fig. 3, some relations between the equilibrium conversion and $H_2O/CO_2$ are shown at several temperatures.

As is shown in Figs. 1—4, a reduction rate of the

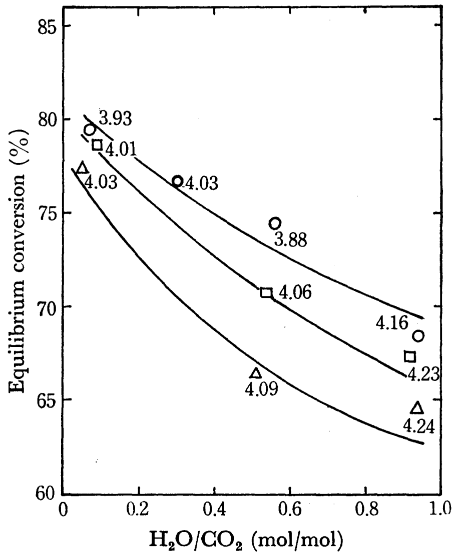

Fig. 3. Effect of $H_2O/CO_2$ on equil. conversion. Each suffix shows $NH_3/CO_2$
-□- 176.5°C, -○- 196.5°C, -△- 216.5°C

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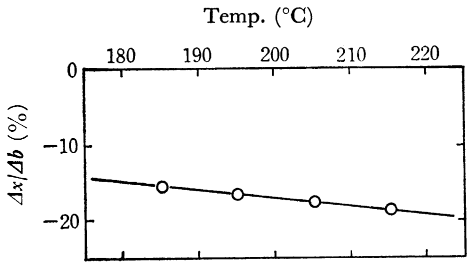
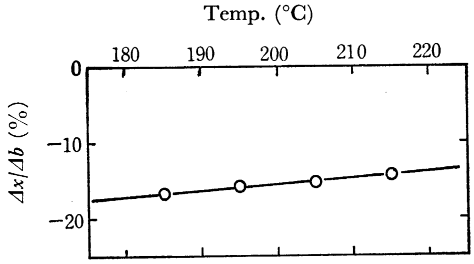
[4] When volumetry by $CO_2$ gas evolution by means of conc. $H_2SO_4$ is used, the error caused by the hydrolysis of urea becomes a problem.



by Eq. (4) (Authors) at $NH_3/CO_2=4$



by Eq. (1) (Frèjacques) at $NH_3/CO_2=4$

Fig. 4. Temperature dependence of reduction rate of equil. conversion.

equilibrium conversion per 1.0 of $\Delta b$ becomes larger when the temperature rises, while, on the contrary, it gradually becomes smaller in Frèjacques' case.

Therefore, the ratio, $R_F$, is rather larger than 100% at higher $H_2O/CO_2$ ratios when the temperature is low, but, inversely, it is smaller when the temperature is high. The inversion temperature lies around 200°C.

*Effect of Temperature* (*Cf.* Fig. 5): This is the most important finding in this report. The equilibrium conversion has its maximum value at a temperature which lies between 190 and 195°C when $NH_2/CO_2$ is about 4.

Therefore, the observed equilibrium conversion is higher than that of Frèjacques at temperatures lower than about 200°C, while, on the contrary, it is lower at temperatures higher than 200°C.

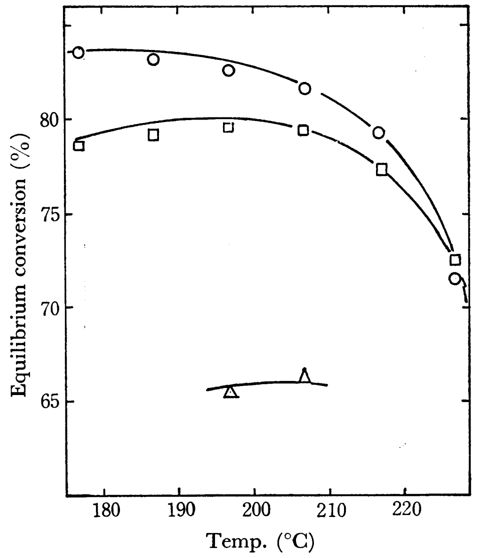


Fig. 5. Effect of temperature on equil. conversion.

| | $NH_3/CO_2$ | $H_2O/CO_2$ |
|---|---|---|
| -△- | Ca 3.1 | Ca 0.38 |
| -□- | Ca 4.0 | Ca 0.05 |
| -○- | Ca 5.0 | Ca 0.12 |

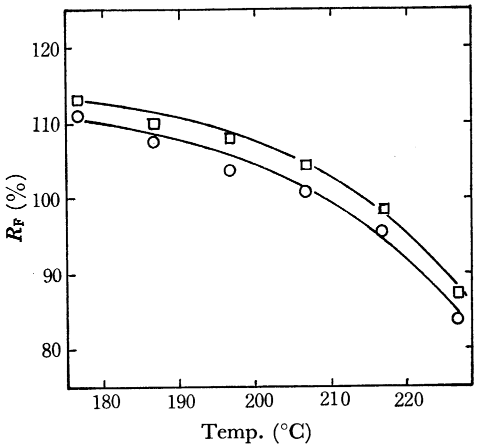


Fig. 6. Effect of temperature on $R_F$

| | $NH_3/CO_2$ | $H_2O/CO_2$ |
|---|---|---|
| -□- | Ca 4.0 | Ca 0.05 |
| -○- | Ca 5.1 | Ca 0.12 |

In Fig. 6 the ratio, $R_F$ of our conversion to that of Frèjacques at the equilibrium state is shown; the figure shows that the equilibrium conversion is higher by 5—15% under the conventional conditions of urea synthesis.

When $NH_3/CO_2$ changes to 5.0, the temperature giving the maximum equilibrium conversion seems to lie lower than 190°C.

*By-products.* It has been reported that the decrease in the equilibrium conversion is also due to the increased formation of by-products,[1] *e.g.*, biuret and cyanuric acid, besides the effect of the loading density. It is thought that this can, to some extent, be prevented by the addition of a large amount of excess $NH_3$; in order to confirm this, we determined the above by-products qualitatively or quantitatively. We found that biuret increases a little at higher temperatures and at lower $NH_3/CO_2$ ratios, but that, under other conditions, the quantity is far from that quantity which corresponds to the reduction of the equilibrium conversion, while no substantial amounts of cyanuric acid and melamine were detected. Furthermore, the amount of total carbon at the loading of materials was nearly equal to that indicated by analyzed value. Therefore, it can be concluded that the reduction of the equilibrium conversion is not due to the by-product formation.

TABLE 2. EFFECT OF LOADING DENSITIES ON THE EQUILIBRIUM CONVERSION

| | A | B | C |
|---|---|---|---|
| Loading density $\gamma$(g/cc) | 0.8 | 0.5 | 0.3 |
| Temp. (°C) | 176.5 | 206.5 | 209.3 |
| Press. (kg/cm²G) | 152.0 | 245.0 | 231.0 |
| $NH_3/CO_2$ (mol/mol) | (5.05)[a)]<br>5.00 | (4.25)[a)]<br>3.98 | (6.0)[a)]<br>4.82 |
| $H_2O/CO_2$ (mol/mol) | 0.08 | 0.42 | 0.04 |
| Conv. obsd (%) | 83.6 | 73.0 | 83.9 |
| Conv. estimated[b)] (%) | 83.2 | 72.8 | 81.5 |

a) Molar ratio of charged $NH_3$ to charged $CO_2$
b) Conversion estimated from those under near conditions at a loading density of $\gamma=0.7$

Table 3. Comparison of equilibrium constant with that of Frèjacques

| Temp (°C) | $NH_3/CO_2$ (mol/mol) | $H_2O/CO_2$ (mol/mol) | $K_{\text{Frèjacques}}$ | $K_{\text{obsd}}$ |
|---|---|---|---|---|
| 176.5 | 4.06 | 0.53 | 1.142 | 2.096 |
| | 4.99 | 0.86 | | 2.353 |
| 196.5 | 4.03 | 0.30 | 1.561 | 2.593 |
| | 5.36 | 0.39 | | 2.069 |
| 216.5 | 4.09 | 0.51 | 2.149 | 1.501 |
| | 5.17 | 0.90 | | 1.241 |

*Effect of the Loading Densities.* As our data were based on the direct sampling from the liquid phase, it is thought that there is no effect of the loading density on the equilibrium conversion. However, in order to confirm this, some experiments with various loading densities were carried out; the results were nearly independent of the loading densities, as is shown in Table 2.

We also reconfirmed the existence of the temperature giving the maximum conversion using a continuous autoclave which was substantially filled with a urea solution.

*Equilibrium Constant.* According to the trends of our data, which are very different from the equation reported by Frèjacques, it is natural that the equilibrium constant obtained by Eq. (1) is also different from that of Frèjacques. Some examples are shown in Table 3.

*Effect on Processes.* From the above-mentioned results, no increase in the equilibrium conversion by raising the temperature can be expected; luckily, the urea reactors were operated at the temperature about 190°C for other reasons—to solve the problems of the reactor materials, pressure, the excess of $NH_3$, *etc.*

We think that the good equalities between the conversion in the process and that in Frèjacques' equation were due to such factors as the structure of the reactors and the operating conditions.

From another point of view, this means that actual conversion can approach equilibrium if we add some device to the reactor.

Of course economic considerations are necessary, and in this connection the design of the urea reactor would be assisted by reaction kinetics engineering.

## Expansion of the Equation of the Equilibrium Conversion

As the equilibrium constant is also affected by the $NH_3/CO_2$ composition, a simple calculation from a equation like Eq. (1) is impossible. Therefore we obtained Eq. (4) by expansion with respect to $a$, $b$, and $t$, taking the character of our results into consideration. Thus, $x$ is expressed:

$$x = C_1a + C_2a^2 + C_3ab + C_4b + C_5a\left(\frac{t}{100}\right) + C_6b\left(\frac{t}{100}\right) + C_7\left(\frac{t}{100}\right) + C_8\left(\frac{t}{100}\right)^3 + C_9 \qquad (4)$$

Where $C_i$ is a factor which was determined by the method of least squares using the data in Table 1. Each $C_i$ value thus obtained is shown in Table 4.

Table 4. $C_i$'s of Eq. (4)

| | | | |
|---|---|---|---|
| $C_1$ | 0.2616 | $C_6$ | −0.1030 |
| $C_2$ | −0.01945 | $C_7$ | 1.640 |
| $C_3$ | 0.0382 | $C_8$ | −0.1394 |
| $C_4$ | −0.1160 | $C_9$ | −1.869 |
| $C_5$ | −0.02732 | | |

By $\partial x/\partial t=0$, the temperatures giving the maximum conversion are, found to be 192°C, 190°C, and 189°C for $a=3$, 4, and 5 respectively, where $b=0$ in all cases.

The differences between the calculated and the observed equilibrium conversions are within 2% in absolute error in 80% of all the data, as is shown in Fig. 7. Therefore, Eq. (4) is useful enough for a simple estimation of the equilibrium conversion.

Although the higher $a$ is, the lower the said temperature seems to be, according to the above values, this is not certain because the data for low $a$ values are few.

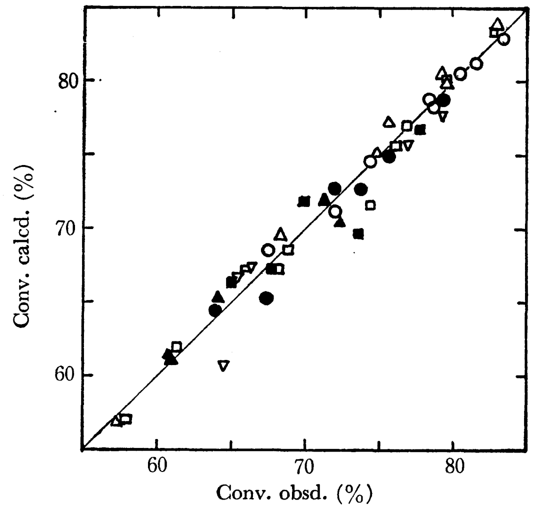


Fig. 7. Comparison of calcd. values with observed values for equil. conversion.

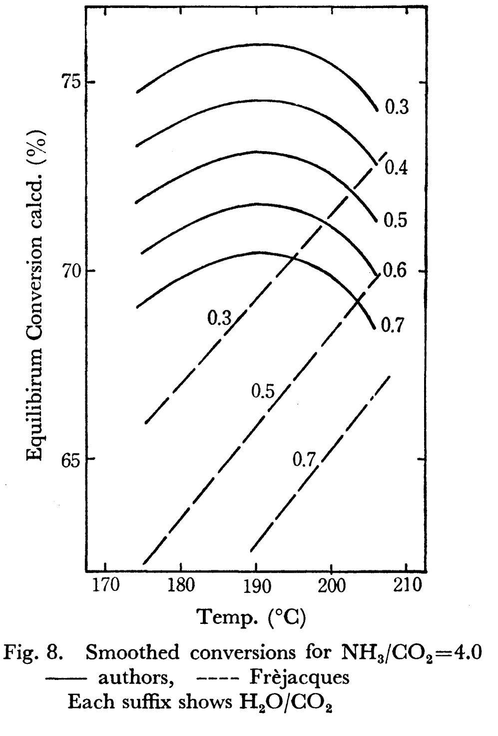


Fig. 8. Smoothed conversions for $NH_3/CO_2=4.0$
—— authors, ---- Frèjacques
Each suffix shows $H_2O/CO_2$

Table 5. Comparison of equilibrium conversions by various equations

| $t$ °C | $a$ | $b$ | $x$ by | | |
|---|---|---|---|---|---|
| | | | Ref. (1)[a] | Ref. 5[b] | Eq. (4) |
| 180 | 3.0 | 0.5 | 53.0 | 58.6 | 63.9 |
| 180 | 5.0 | 0.5 | 69.5 | 75.6 | 79.1 |
| 180 | 4.0 | 1.0 | 54.4 | 61.6 | 66.0 |
| 180 | 5.0 | 1.0 | 63.5 | 70.2 | 73.5 |

a) Values obtained by means of Frèjacques' monograph
b) Experimental values in Ref. 5

If this is true, however, it is a very interesting phenomenon.

An attempt like Eq. (4) was reported in Ref. 5 (*cf.* Eq. (5)), but the equilibrium conversion of this report lies between our data and those of Frèjacques; some examples are shown in Table 5. We suppose that the difference is due to a different experimental method.

The term of pressure in Eq. (5) is substantially not essential, from our point of view. The effects of $NH_3/CO_2$, $H_2O/CO_2$, and the temperature are very similar with our data, but this is supposed to be by chance because the highest temperature in Ref. 5 does not exceed 190°C.

$$\begin{aligned} x = {} & 34.28\,a - 1.770\,a^2 - 29.30\,b + 3.699\,ab \\ & + 0.09129\,t - 0.07482\,at - 5.395\times10^{-6}\,t^3 \\ & + 0.002293\,P - 112.1 \end{aligned} \qquad (5)$$

In Fig. 8 smoothed curves of the equilibrium conversion for the case of $NH_3/CO_2=4.0$ are compared with those of Frèjacques.

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5) V. I. Kucherryavyi, *Khim. Prom.* (3), 200 (1969).