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Equilibrium of Urea Synthesis. II.

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In the preceding paper (This Bulletin, **45**, 1339 (1972)) it was reported that the existence of the maximum equilibrium conversion was not due to the experimental method. For this phenomenon, we have presented the following interpretation. While $NH_4CO_2NH_2$ is converted to urea and water, it dissociates into NH_3 and CO_2 in the solution (not in the gas phase), and the degree of the dissociation increases exponentially as the temperature becomes higher, while the conversion to urea gradually increases. Therefore, at a certain temperature, the equilibrium conversion reaches its maximum value. Although it is nearly impossible to prove analytically the dissociation of $NH_4CO_2NH_2$ in the solution, we are sure of it from the following facts: 1) The dissociation of $NH_4CO_2NH_2$ is a great endothermic reaction, even under the conditions of urea synthesis. 2) The value of NH_3/CO_2 which gives the minimum equilibrium pressure at a usual temperature is not always equal to 2.0, but varies with the temperature. 3) The effect of H_2O/CO_2 on the equilibrium pressure varies with the temperature; that is, when the temperature is lower than about 200°C, an increase in H_2O/CO_2 reduces the equilibrium pressure, but when the temperature is higher than 200°C, an increase in H_2O/CO_2 makes the equilibrium pressure higher.

The dissociation of $NH_4CO_2NH_2$ in a solution has never been proved by means of chemical analysis, because experimentally it is nearly impossible to separate CO_2 in the form of carbamate from free CO_2. This has already been reported in Ref. 1.

However, in view of the fact that we carried out experiments over a broader range than in Ref. 1, many facts may be thought to suggest the dissociation of $NH_4CO_2NH_2$ in the solution. This point will be discussed.

Mechanism of the Equilibrium

In the preceding paper[2] we reported that the equilibrium conversion is independent of the loading density if the composition in the liquid phase is constant; therefore, other points must be investigated.

Our interpretation is that part of the $NH_4CO_2NH_2$ dissociates into NH_3 and CO_2 in the solution, and that this causes the temperature which gives the maximum equilibrium conversion. Thus, we presume two kinds of chemical equilibria in the solution, as is shown in Eqs. (1) and (2):

$$NH_4CO_2NH_2(\text{soln}) \rightleftarrows 2NH_3(\text{soln}) + CO_2(\text{soln}) \quad (1)$$

$$NH_4CO_2NH_2(\text{soln}) \rightleftarrows (NH_2)_2CO(\text{soln}) + H_2O(\text{soln}) \quad (2)$$

The equilibrium constants, K_1 and K_2, are defined as follows (the solutions are assumed to be ideal);

$$K_1(T) = \frac{x^2_{NH_3} \cdot x_{CO_2}}{x_{\text{carb}}} \quad (3)$$

$$K_2(T) = \frac{x_u \cdot x_{H_2O}}{x_{\text{carb}}} \quad (4)$$

The equilibrium constant, $K_F(T)$, for the Frèjacques equation then becomes:

$$K_F(T) = \frac{K_2(T)}{K_1(T)} = \frac{x_u \cdot x_{H_2O}}{x^2_{NH_3} \cdot x_{CO_2}} \quad (5)^{3)}$$

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[1] S. Kawasumi, *Journal of the Society of High Pressure Gas Industry*; **20**, No. 2, 4 (1956).

[2] S. Inoue, K. Kanai, and E. Otsuka, **45**, 1339 (1972).

[3] Although Eq. (5) is apparently the same as the Eq. (1) of Frèjacques reported in the previous paper, $K_F(T)$ is not equal to $K(t)$, because the molar fractions for each component are not equal in the two equations.

where x_{NH_3}, x_{CO_2}, x_u, x_{H_2O}, and x_{carb} denote the molar fractions of NH_3, CO_2, urea, H_2O, and carbamate respectively.

If $K_1(T)$ increases exponentially above a certain temperature compared with $K_2(T)$, as is shown in Fig. 1, the equilibrium constant, $K(t)$, in the previous paper reaches its maximum value near the temperature which results in the maximum equilibrium conversion.

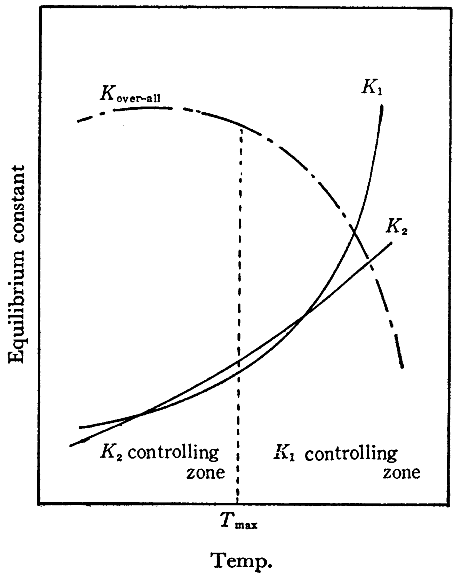

Fig. 1. Temperature dependence of $K_1(T)$, $K_2(T)$, and overall equilibirum constant.

Besides this, there is another presumption that when the urea formation of Eq. (2) change from an endothermic to an exothermic reaction at a certain temperature, the equilibrium conversion reaches its maximum value according to the Van't Hoff equation, because a high temperature—for example, 200°C—can not be easily attained in the urea reactor if the degree of dissociation of $NH_4CO_2NH_2$ is so large. However, our presumption seems to be true, judging from the following evidence.

Thermodynamic Discussion

Let the liquid composition be as follows before and after the reaction:

$$2NH_3 + CO_2 \underset{}{\overset{K_1(T)}{\rightleftarrows}} \text{carb} \overset{K_2(T)}{\rightleftarrows} \text{urea} + H_2O \tag{6}$$

before the reaction:

$$2m_N,\ 1,\ 0,\ 0,\ m_H,$$

after the reaction:

$$2(m_N - m_K - m_u),$$
$$m_c,\ m_K,\ m_u,\ m_u + m_H$$
$$\therefore\ \text{total} = 2m_N - 1 + 2m_c + m_u + m_H$$
$$(\because\ m_c + m_K + m_H = 1)$$

$$K_1(T) = \frac{(4m_N - 1 + m_c)^2 \cdot m_c}{(2m_N - 1 + 2m_c + m_u + m_H)^2(1 - m_u - m_c)} \tag{7}$$

$$K_2(T) = \frac{m_u(m_u + m_H)}{(2m_N - 1 + 2m_c + m_u + m_H)^2(1 - m_u - m_c)} \tag{8}$$

If it is assumed that $K_1(T)$ and $K_2(T)$ are dependent only on the temperature, the equilibrium conversion, m_u, can be obtained by solving Eqs. (7) and (8) at given NH_3/CO_2 ($=2m_N$) and H_2O/CO_2 ($=m_H$) ratios. Therefore, the temperature, T_{max}, giving the maximum equilibrium conversion is obtained by solving:

$$dm_u/dT = 0$$

However, neither m_c nor m_u is separable from the other in Eqs. (7) and (8), so it is difficult to obtain the derivative in a simple form.

On the other hand, it is doubtful whether or not the system or urea synthesis can be assumed to be ideal; therefore, we will show only the existence of the maximum conversion, using a simple model in the case of simultaneous equilibria.

Thus, let the following system be taken:

$$A \overset{K_A}{\rightleftarrows} C \overset{K_B}{\rightleftarrows} B$$
$$a,\ 1-a-b,\ b,\ \text{total} = 1\ \text{mol}$$

$$K_A = \frac{a}{1-a-b} \tag{9}$$

$$K_B = \frac{b}{1-a-b} \tag{10}$$

From Eqs. (9) and (10),

$$A = \frac{K_A(T)}{K_B(T)} \cdot b$$

We thus obtain:

$$b = \frac{K_B(T)}{1 + K_A(T) + K_B(T)} \tag{11}$$

As b is dependent only on the temperature, the differentiation of b with respect to T affords:

$$K_B'(T)(1 + K_A(T)) = K_B(T) \cdot K_A'(T) \tag{12}$$

Within a relatively narrow range of temperature, $K_A(T)$ and $K_B(T)$ may be expressed as follows:

$$A_0 - A_1 T = -RT \ln K_A,\ B_0 - B_1 T = -RT \ln K_B \tag{13}$$

By the substitution of K_A and K_B in Eq. (12) with Eq. (13), and by solving Eq. (12) with respect to T, the temperature, T_{max}, giving the maximum conversion is obtained:

$$T_{max} = \frac{A_0}{R\left(\frac{A_1}{R} - \ln \frac{B_0}{A_0 - B_0}\right)} \tag{14}$$

where $A_0 > B_0 > 0$.

If the logarithmic term is very small compared with the A_1/R, term:

$$T_{max} \div A_0/A_1 \tag{15}$$

Therefore, T_{max} can be calculated if A_0, A_1, and B_0 are given. Now,

$$\Delta G = \Delta H - T\Delta S$$

By assuming ΔH and ΔS to be constant within a narrow range of temperature, A_0 or B_0 is replaced by ΔH, and also A_1 or B_1, by ΔS. Therefore, if ΔH and ΔS are given, T_{max} can be calculated.

Although it is very difficult to estimate these real values under the conditions of urea synthesis, if the values in Ref. 1 can be used, T_{max} can be obtained; that is,

$$A_0 = 15890,\ A_1 = 33.7,\ B_0 = 9160$$

$$\therefore\quad T_{\max} = \frac{15890}{33.7 - 4.575 \log 1.36} = 482°\mathrm{K} \tag{16}$$

$$\therefore\quad t_{\max} = 209°\mathrm{C}$$

The value of $T_{\max}$ thus obtained is a little different from the actual one. This inconsistency is unavoidable in such a simple treatment.

We estimate the heat of dissociation of $NH_4CO_2NH_2$ in the solution at the temperature of urea synthesis, using a thermochemical cycle from the standard state of $NH_4CO_2NH_2$. It decreases with the rise in the temperature, but it does not turn out to be zero or minus, as is shown in Table 1. Therefore, it may be presumed that the dissociation of $NH_4CO_2NH_2$ in the solution takes place.

TABLE 1. HEAT OF DISSOCIATION OF $NH_4CO_2NH_2$ (Estimated)

Temp	°C	160	180	200	220
ΔH	cal/mol	27074	24746	21993	20509

On the other hand, assuming that $K_1(T)$ and $K_2(T)$ are expressed as in Eq. (13), a value for A_0, which is approximately equal to the heat of the dissocation of $NH_4CO_2NH_2$ can be obtained in such a way that the optimum values of A_0, B_0, A_1, and B_1 are selected; the difference between the calculated and the observed conversion thus becomes a minimum when Eqs. (7) and (8) are solved simultaneouly for some given data. The value thus estimated is about 20 kcal/mol $NH_4CO_2NH_2$.

Discussion of the Equilibrium Pressure

The Minimum Equilibrium Pressure. The effect of NH_3/CO_2 (mol/mol) on the equilibrium pressure is shown in Fig. 2, where curves are drawn assuming a smoothed formula.

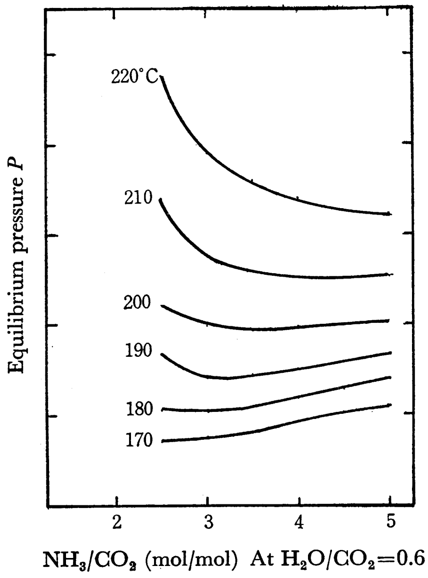

Fig. 2. Effect of NH_3/CO_2 on the equilibrium pressure.

The minimum equilibrium pressure at any temperature under the usual conditions of urea synthesis does not exist at 2.0 of NH_3/CO_2; as the temperature rises, the minimum point seems to move to higher values of NH_3/CO_2. Furthermore, the effect of NH_3/CO_2 on the equilibrium pressure at higher temperatures becomes slightly sensitive.

TABLE 2. PARTIAL PRESSURES OF NH_3 AND CO_2

Component	NH_3[a]	CO_2[b]	$NH_4CO_2NH_2$[c] ($2NH_3+CO_2$)
mol/mol H_2O	1.0	0.022	1.0
Partial press. kg/cm²abs.	32.5	200	8.7 (5.8+2.9)

(at 120°C)

a) observed value by authors

b) Seidel's data collection

c) Calculated value by Raoult's law applied to the dissociation pressure by Frèjacques.

This can be understood according to the following explanation. Table 2 shows each partial pressure when NH_3, CO_2, or carbamate dissolves into one mole of H_2O.

It is evident that the partial pressure of CO_2, p_{CO_2}, is much greater than that of any other component because of physical absorption. As the partial pressure of H_2O, p_{H_2O}, is small compared to the total pressure, P: according to the mass action law and Raoult's law, the following equation is obtained:

$$P \doteqdot p_{NH_3} + p_{CO_2} \tag{17}$$

Then, by combining Eq. (17) with Eq. (18), Eq. (19) is obtained:

$$K_P(T) = (f_N p'_{NH_3})^2 (f_c p'_{CO_2}) \tag{18}$$

where p_{NH_3} and p_{CO_2} are actual partial pressures, and where p'_{NH_3} and p'_{CO_2} are ideal partial pressures;

$$P \doteqdot f_N p'_{NH_3} + K_P(T)/(f_N p'_{NH_3})^2 \tag{19}$$

therefore, f_N and f_C are factors which inidcate deviation from an ideal solution. By the partial differentiation of Eq. (19) with respect to p'_{NH_3}, Eq. (20) is obtained:

$$\frac{\partial P}{\partial p'_{NH_3}} = \frac{\partial f_N}{\partial p'_{NH_3}} \cdot p'_{NH_3} + f_N - 2\left(\frac{f_c p_{CO_2}}{f_N} \cdot \frac{\partial f_N}{\partial p'_{NH_3}} + \frac{f_c p'_{CO_2}}{p'_{NH_3}}\right) \tag{20}$$

Now, by supposing that f_N is independent of the p'_{NH_3}-compositions in the solution, and that $\partial f_N/\partial p'_{NH_3}=0$, at the minimum pressure, Eq. (20) becomes Eq. (21):

$$\frac{\partial P}{\partial p'_{NH_3}} = f_N - 2\frac{f_c p'_{CO_2}}{p'_{NH_3}} = 0 \tag{21}$$

$$p'_{NH_3}/p'_{CO_2} = 2 f_c/f_N \tag{22}$$

As p'_{NH_3}/p'_{CO_2} is the ratio of the partial pressure of NH_3 to that of CO_2 in equilibrium with the solution, this is also the molar ratio of NH_3 to CO_2 in the solution. When we think that NH_3 dissolves by chemical absorption, while CO_2 dissolves by physical absorption, $f_c \gg f_N$.

Since NH_3/CO_2, which gives the minimum equilibrium pressure, is greater than 2, and since the effect

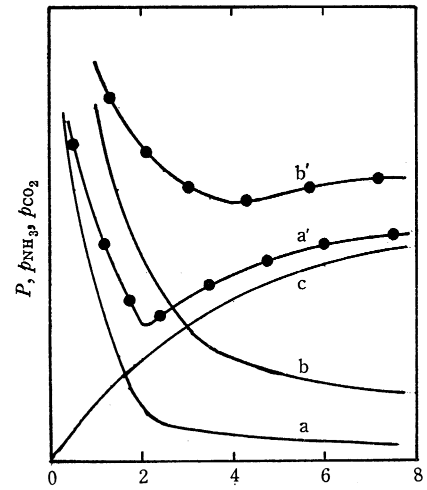

Fig. 3. Partial and total equilibrium pressure profile *vs.* NH_3/CO_2.
at const. temperature
a: p_{CO_2}, a′: P when $f_C=f_N$
b: p_{CO_2}, b′: P when $f_C>f_N$
c: p_{NH_3} of NH_3aq.

of the temperature on f_c is much greater than that on f_N, when the temperature becomes higher, the minimum equilibrium pressure moves to the side of higher NH_3/CO_2 ratios, we think.

If $NH_4CO_2NH_2$ does not dissociate into NH_3 and CO_2, and if the system is assumed to be ideal, the equilibrium pressure naturally reaches its minimum value when NH_3/CO_2 is just equal to 2. Figure 3 indicates the above state schematically.

However, NH_3 and CO_2 in the solution partially neutrallize each other, so p_{NH_3} and p_{CO_2} may be considered to be greatly reduced. Furthermore, the urea which is contained in the solution of urea synthesis is also a solvent for NH_3 and carbamate, so p_{NH_3} and p_{CO_2} are lower than in the case of no urea. From these considerations, the actual equilibrium pressure can be said not to be so great as was estimated from such data as those in Table 2.

Effect of H_2O/CO_2. While the increase in H_2O/CO_2, a solvent for carbamate, brings about a lowering of the equilibrium pressure, it also lowers the amount of urea to be formed, and urea is also a solvent for carbamate. Therefore, it is thought that the equilibrium pressure remains almost unchanged, or is reduced to some extent, with the increase in H_2O/CO_2, depending on the temperature.

The experimental data, however, show that, at a lower temperature, the equilibrium pressure is gradually reduced as H_2O/CO_2 increases and that, on the contrary, at a temperature higher than 200°C, it increases as H_2O/CO_2 increases (*cf.* Table 1 in the preceding paper).

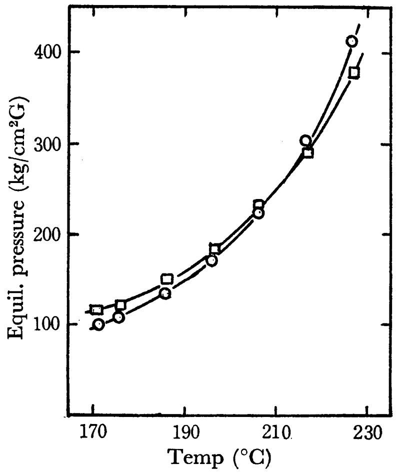

Fig. 4. Temperature dependence of the equilibrium pressure at various H_2O/CO_2.
at $NH_3/CO_2 \doteqdot 4$
-□- $H_2O/CO_2 \doteqdot 0.1$ -○- $H_2O/CO_2 \doteqdot 0.9$

Some examples are shown in Fig. 4. For this phenomenon we have the following interpretation. That is, when the temperature is low, the equilibrium pressure stays almost constat, or is reduced, with an increase in H_2O/CO_2 because of the low degree of dissociation of $NH_4CO_2NH_2$ in the solution.

When the temperature is high, however, the equilibrium pressure becomes higher because of the high degree of dissociation of $NH_4CO_2NH_2$ in the solution,[4] because the partial pressures of free NH_3 and CO_2 are much greater than the partial pressure of $NH_4CO_2NH_2$ in the solution.

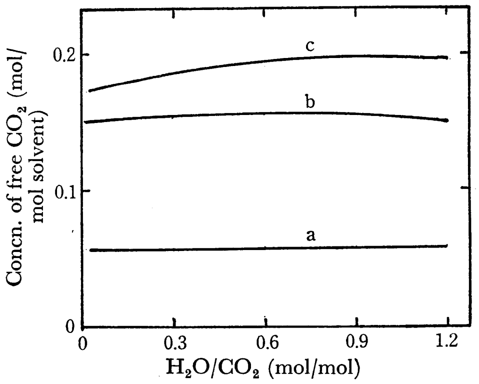

Fig. 5. Effect of H_2O/CO_2 on the conc. of free CO_2 in the solution.
a: 160°C, b: 190°C, c:220°C

The authors owed much computational aid to Mr. Kenji Yoshida. Here we gratefully acknowledge him.

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[4] Figure 5 shows the concentration of free CO_2 in the solution due to the dissociation of $NH_4CO_2NH_2$, when the solvent effect of formed urea are taken into consideration.