Equilibrium of the CO_2-NH_3-Urea-H_2O System under High Temperature and Pressure. IV.

Effect of Loading NH_3-CO_2 Mole Ratio on Equilibrium Pressure and Vapor Composition

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In 1918 Fichter, Steiger and Stanisch(1) found ammonia to exert a beneficial influence for the formation of urea from ammonium carbamate only when moderate amounts were used in their experiment in which they heated ammonium carbamate with ammonia. H. J. Krase and V. L. Gaddy(2) later obtained the yield of urea of 80 to 85% calculated on ammonium carbamate initially charged in the presence of as much as 300% excess ammonia at a temperature of 155°C. They explained that an excess amount of ammonia over that combined as carbamate acts as a dehydrating agent, removing the water from the active mass, thus preventing its reaction with urea and thereby shifting the equilibrium toward the urea side. They found also that an excess amount of carbon dioxide added to carbamate exerts no such effect. In the same way, Hori and Ogami(3) investigated the yield of urea in the presence of excess ammonia over the temperature range from 130° to 180°C. and found excellent agreement with the mass law according to the equation:

$$CO_2+2NH_3 \rightleftharpoons CO(NH_2)_2+H_2O \qquad (1)$$

However, the equilibrium constant of the equation (1) employed by them was represented by mole fraction derived from the initial loading composition and the yield of urea without distinction between the liquid- and vapor-compositions. It is evident that the liquid-vapor phase equilibrium of the system is dependent upon the loading density of the initial content in the reaction vessel in the presence of excess ammonia or carbon dioxide as well as in the stoichiometrical loading mole ratio of $2NH_3$ to $1CO_2$.(4)

No one, to my knowledge, has shown the effect of excess ammonia or carbon dioxide added to ammonium carbamate on the liquid and vapor phase equilibrium. The effects of the variation of the loading mole ratio of ammonia to carbon dioxide over the range from 1.60 to 3.40 on the equilibrium pressure and the composition of the vapor phase are described in this paper.

Experimental Procedure

The equilibrium pressure and the composition of the vapor phase were respectively determined

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(1) Fichter, Steiger and Stanisch, *Verhandl. Naturforsch. Ges. Basel*, **28**, II, 66 (1918); *Chem. Abst.*, **14**, 540 (1920).

(2) H. J. Krase and V. L. Gaddy, *J. Am. Chem. Soc.*, **52**, 3088 (1930).

(3) Hori and Ogami, *J. Soc. High Pressure Gas Ind. Japan*, **6**, 256 (1942).

(4) S. Kawasumi, This Bulletin, **24**, 148 (1951).

with the methods reported in the previous papers(4)(5) after heating the reaction vessel at 160°C. for 20 to 24 hours. The starting materials were prepared by loading ammonium carbamate or equi-molar urea and water into the reaction vessel with a constant loading density of 0.60 g./cc., followed by the addition of the required amounts of liquid ammonia or solid carbon dioxide to it by the procedure described below. Consequently, the total loading density including excess liquid ammonia or solid carbon dioxide was more than 0.60 g./cc. The amount of liquid ammonia and solid carbon dioxide added to one mole of carbamate ranged from 0.10 to 1.40 moles and from 0.10 to 0.25 moles, respectively. In other words, the range of the loading mole ratio of ammonia to carbon dioxide covered in the present study was 1.60 to 3.40.

Procedure for Loading Liquid Ammonia:—Loading of excess liquid ammonia was accomplished by a special method measuring its weight directly without such a steel weighing pipette as employed by Krase and Gaddy,(2) or steel bomb equipped with a liquid level indicator in order to measure its volume as usually employed. Ammonium carbamate or equi-molar urea and water was weighed out accurately in a glass beaker, as large as the reaction vessel can hold as shown in Fig. 1, which was put on the left pan of the balance. After the balance weight equivalent to the required amount of liquid ammonia to be added to carbamate was put on the right pan, liquid ammonia withdrawn previously from its bomb in an open vessel was poured on the above content in the glass beaker on the left pan. Since the vaporisation of ammonia initially charged induces the cooling of the glass beaker and its content due to the latent heat of the vaporisation, it is possible to charge a required amount of liquid ammonia, accurately, into the beaker. This mixture was introduced into the reaction vessel together with the beaker, and then the vessel was closed as quickly and securely as possible, to prevent the loss of material by leakage. If the procedure was finished within a few minutes, only a negligibly small quantity of gaseous ammonia was lost during the above manipulation.

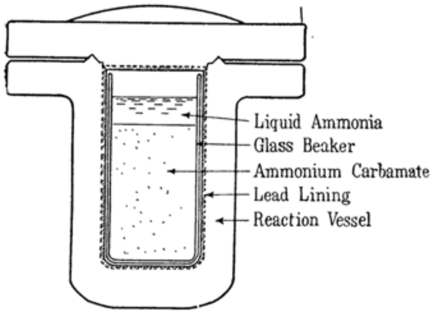

Fig. 1.—Experimental apparatus.

Procedure for Loading Solid Carbon Dioxide:—A required quantity of solid carbon dioxide was weighed out and then as soon as it was introduced into the reaction vessel in which ammonium carbamate was previously charged, the reaction vessel was closed as quickly as possible.

Experimental Results and Discussion

Relation between Equilibrium Pressure and Loading Composition:—The effect of the loading mole ratio of ammonia to carbon dioxide (L) on the equilibrium pressure (P) has been investigated at a temperature of 160°C. from several starting materials, which were prepared by adding liquid ammonia or solid carbon dioxide respectively to ammonium carbamate only, an equi-molar mixture of urea and water, or an equi-molar mixture of carbamate, urea and water which were loaded at a constant density of 0.60 g./cc. in each case.

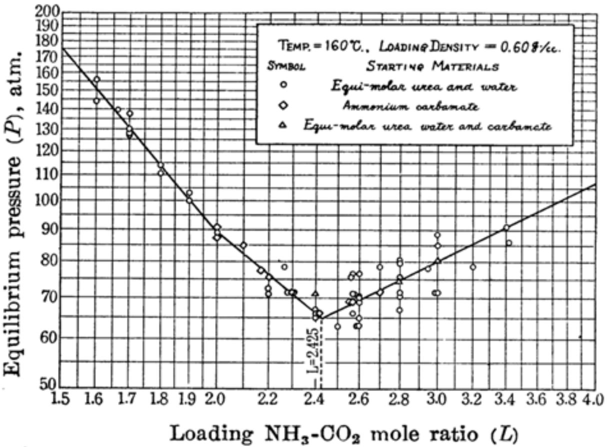

Fig. 2.—Equilibrium pressure of the CO_2-NH_3-Urea-H_2O system in the presence of excess ammonia or carbon dioxide at 160°C.

The results of these experiments are shown by three straight lines as a plot of the logarithm of P against the logarithm of L in Fig. 2. The equilibrium pressure rises up with increasing the excess amount of carbon dioxide and it reaches 150 atmospheres at a loading mole ratio $L=1.60$. No one, to my knowledge, has shown the relation between P and L, and yet it has usually been conjectured that the same pressure rise may be observed with increasing the excess amount of ammonia.

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(5) S. Kawasumi, This Bulletin, **25**, 227 (1952).

Dr. S. Kodama,⑹ Professor of Kyoto University, however, suggested three years ago that the equilibrium pressure had a tendency to decrease with excess ammonia, when it was added to ammonium carbamate, to the minimum. The present measurements at 160°C. have also shown the system definitely to exert the minimum pressure at a loading mole ratio $L=2.43$. The reason why the minimum pressure is caused by the addition of excess ammonia is explained in the following section. The results of these experiments are represented by three empirical equations as shown in Table 1. A discontinuous point at a loading mole ratio of $2NH_3$ to $1CO_2$, where only carbamate or equi-molar urea and water were initially loaded in the reaction vessel, may possibly be attributed to the fact that the total loading density is minimum at this point.

Table 1

Empirical Equations for the Equilibrium Pressure of the CO_2-NH_3-Urea-H_2O System in the Presence of Excess Ammonia or Carbon Dioxide at 160°C. and $D=0.60$ g./cc.

Range of L	Empirical Equation
1.60—2.00	$P=459.5\,L^{-2.372}$
2.00—2.43	$P=273.4\,L^{-1.618}$
2.43—3.40	$P=26.75\,L$

where P= pressure, atm. and L= loading mole ratio of NH_3 to CO_2

Relations between the equilibrium pressure and the loading composition over the temperature range from 130° to 190°C. are shown in Fig. 3. These experiments were performed with the initial mixtures of equi-molar urea and water and excess ammonia. The loading mole ratio of ammonia to carbon dioxide at which the system exerts the minimum equilibrium pressure varies from 2.4 to 2.5 with the rise of temperature from 130° to 190°C. as indicated by a broken line in Fig. 3.

Relation between Vapor Composition and Loading Composition:—Mole ratios of ammonia to carbon dioxide (R') and of water to carbon dioxide (S') in the vapor phase in the equilibrium with the liquid phase have been determined at a temperature of 160°C. and over the range of the loading mole ratio $L=1.60$ to 3.40. A plot of the logarithm of the measured mole ratios of R' and S' against the logarithm of L is respectively shown in Fig. 4, in which $R'-L$ relation at 160°C. is represented by the following equation.

$$R'=L^{6.764}/2\times10^2.$$

At $L=2.43$ where the system exerts the minimum equilibrium pressure at 160°C. as

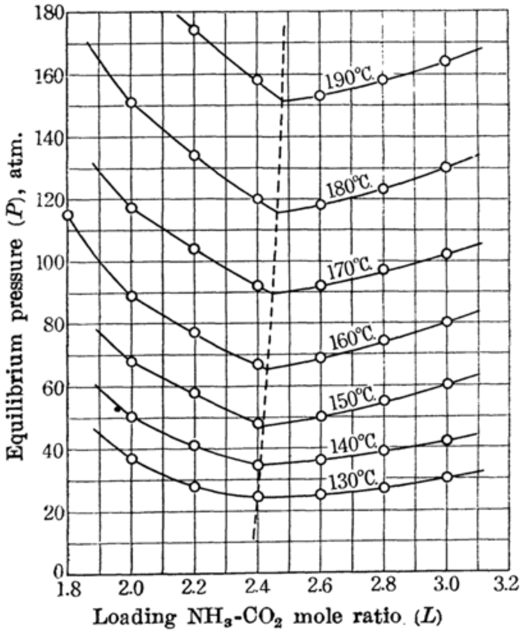

Fig. 3.—P-L-T relations of the CO_2-NH_3-Urea-H_2O system

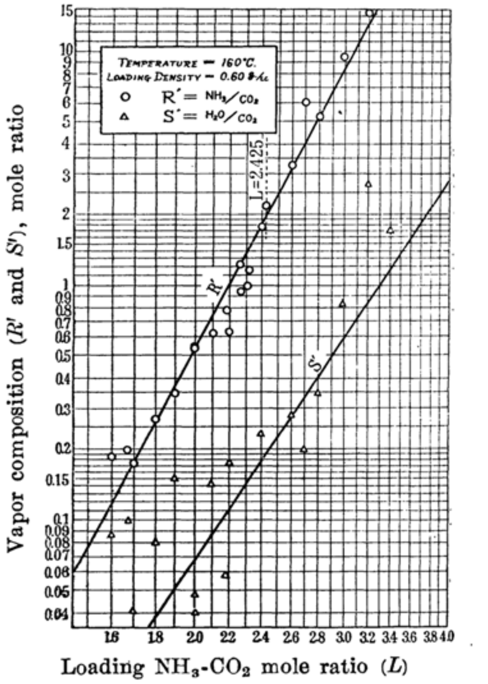

Fig. 4.—Vapor composition of the CO_2-NH_3-Urea-H_2O system in the presence of excess ammonia or carbon dioxide at 160°C.

⑹ S. Kodama, *Unpublished report at Research Department, Nissin Chem. Co.* (1950).

pointed out in the preceding section, definitely $R'=2.00$, that is to say, the mole ratio of ammonia to carbon dioxide in the vapor phase is equivalent to the composition of ammonium carbamate.

Relation between Vapor Cmposition and Equilibrium Pressure :—For the purpose of studying the relation between the vapor composition and the equilibrium pressure, the partial pressures of each of the components (p_{CO_2}, p_{NH_3} and p_{H_2O}) in the vapor phase under several conditions have been calculated from the previous investigations of the author(4),(5) assuming the vapor to be a perfect gas. Table 2∼4 show respectively the variations of the partial pressure with the temperature at a constant loading density (D) of 0.60 g./cc., the variation with the loading density of ammonium carbamate in the absence of excess ammonia or carbon dioxide, and the variation with the amount of water added to one mole of carbamate (W) at a constant temperature of 160°C. Table 5 shows the results of calculation from the present measurement of the vapor compositions under the conditions of $L=1.6-3.0$, $D=0.60$ g./cc. and 160°C.

According to trial calculations of $K_p=p_{CO_2} p^2_{NH_3} p_{H_2O}$ which are shown in these Tables, the logarithm of K_p is a linear function of the temperature over the range between 140° and 180°C. as shown in Fig. 5, while at a constant temperature of 160°C. $K_p\times10^{-5}$ is

Table 2

Relation between Partial Pressure of the CO_2-NH_3-Urea-H_2O System and Temperature at Constant Loading Mole Ratio $L=2.00$ and Loading Density of 0.60 g./cc.

Temp., °C.	Partial Pressure, atm.			$K_p\times10^{-5}$
	p_{CO_2}	p_{NH_3}	p_{H_2O}	
140	33.4	15.7	1.4	0.115
150	43.7	22.0	2.3	0.486
160	55.2	30.2	3.6	1.81
170	69.9	41.4	5.7	6.83
180	86.1	55.9	9.0	24.2

Table 3

Relation between Partial Pressure of the CO_2-NH_3-Urea-H_2O System and Loading Density at Constant Temp.=160°C. and Loading Mole Ratio $L=2.00$

D, g./cc.	Partial Pressure, atm			$K_p\times10^{-5}$
	p_{CO_2}	p_{NH_3}	p_{H_2O}	
0.20	27.2	37.0	4.5	1.70
0.40	39.9	32.5	4.1	1.73
0.60	55.2	30.2	3.6	1.81
0.80	74.2	30.0	3.3	2.20
1.00	100.6	32.6	3.3	3.53

Table 4

Relation between Partial Pressure of the CO_2-NH_3-Urea-H_2O System and Added Water at Constant Temp.=160°C., Loading Mole Ratio $L=2.00$, and Loading Density $D=0.60$ g./cc.

Added water, mole/mole, carbamate	Partial Pressure, atm.			$K_p\times10^{-5}$
	p_{CO_2}	p_{HN_3}	p_{H_2O}	
0	55.2	30.2	3.6	1.81
0.20	57.0	28.5	3.5	1.62
0.40	58.5	27.0	3.5	1.49
0.60	60.0	25.6	3.4	1.34
0.80	61.3	24.2	3.5	1.26
1.00	62.5	23.1	3.4	1.13

Table 5

Relation between Partial Pressure of the CO_2-NH_3-Urea-H_2O System and Loading Mole Ratio at Constant Temp.=160°C. and Loading Density $D=0.60$ g./cc.

L, Loading mole ratio	Partial Pressure, atm.			$K_p\times10^{-5}$
	p_{CO_2}	p_{HN_3}	p_{H_2O}	
1.60	127.9	19.9	3.2	1.62
1.80	86.0	24.6	3.4	1.77
2.00	55.2	30.2	3.6	1.81
2.20	35.4	36.7	3.9	1.86
2.40	21.8	40.4	3.8	1.35
2.62	15.0	50.6	3.9	1.50
2.80	11.2	59.6	4.2	1.67
3.00	7.4	68.4	4.2	1.46

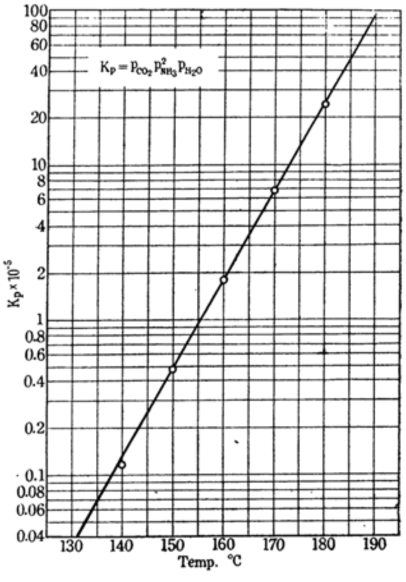

Fig. 5.—K_p-Temp. relation at $L=2$ and $D=0.60$ g./cc.

approximately constant (1.1∼3.5) independent of D, W and L within the range of the present experimental conditions.

The approximate constancy of K_p seems to show that at least for practical purposes the assumption, that the activity of ammonium carbonate in the liquid phase is 1, is allowable. If we take such assumption as ammonium carbonate dissociates according to the equation:

$$(NH_4)_2CO_3(l) \rightleftharpoons CO_2(g)+2NH_3(g)+H_2O(g),$$

the equilibrium constant must be constant as follows.

$$K_p=P^4N'_{CO_2}N'^2_{NH_3}N'_{H_2O}$$
$$\equiv \text{a constant at } 160°C.$$

where P is the total pressure of the system and N_i' is the mole fraction of i-component in the vapor phase.

$$N'_{CO_2}+N'_{NH_3}+N'_{H_2O}=1$$

Accordingly,

$$K_p=P^4N'^2_{NH_3}1(-N'_{NH_3}-N'_{H_2O})N'_{H_2O}$$

Supposing that N'_{H_2O} is constant,

$$\frac{\partial P}{\partial N'_{NH_3}}=\frac{K_p^{1/4}(3N'_{NH_3}+2N'_{H_2O}-2)}{4N'^{3/2}_{NH_3}N'^{-1/4}_{H_2O}(1-N'_{NH_3}-N'_{H_2O})^{5/4}}$$

At a vapor composition where the system exerts the minimum pressure,

$$\frac{\partial P}{\partial N'_{NH_3}}=0$$

Therefore,

$$3N'_{NH_3}+2N'_{H_2O}-2=0$$

or

$$R'\equiv\frac{N'_{NH_3}}{N'_{CO_2}}=2$$

Thus, it has been verified that the mole ratio of ammonia to carbon dioxide in the vapor phase under the minimum pressure of the system at a given temperature is equal to that of ammonium carbamate independent of the amount of water in the vapor.

Effect of Temperature on Relation between Vapor- and Loading Composition: —Mole ratio of ammonia to carbon dioxide in the vapor phase (R') has also been determined at 140° and 180°C. as well as 160°C. over the range of the loading mole ratio $L=2.0-3.0$.

The experimental results and empirical equations for $R'-L$ relations are given in Fig. 6. These three straight lines intersect at a

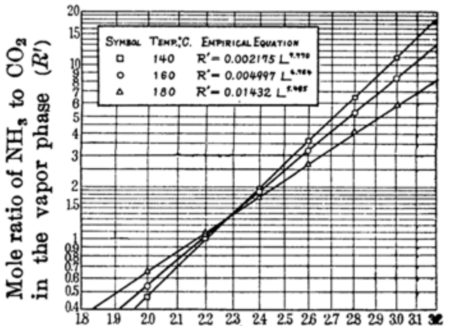

Fig. 6.—R'-L relations at 140°, 160° and 180°C.

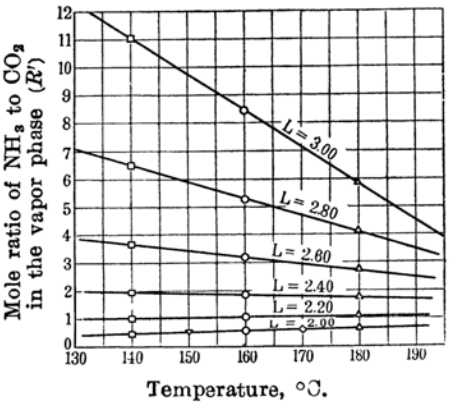

Fig. 7.—Relation between mole ratio of NH_3-CO_2 in the vapor phase and temperature over the range of $L=2\sim3$

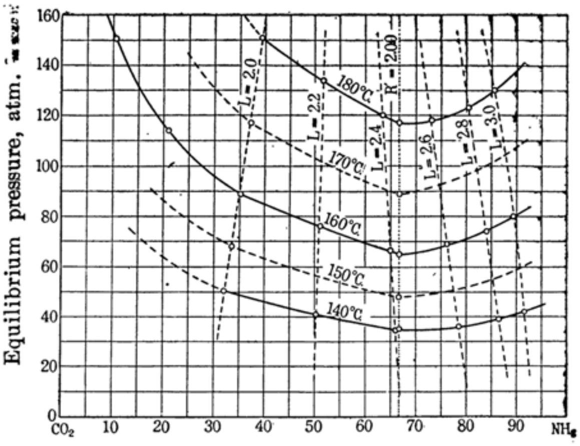

Fig. 8.—Equilibrium pressure-vapor composition diagrams for the CO_2-NH_3-Urea-H_2O system

point near $L=2.28$, where R' is constant independent of temperature. R' is also a linear function of temperature at a given loading composition as shown in Fig. 7.

From the above data, such a relation as shown in Fig. 8 is derived between the equilibrium pressure and ratio of ammonia to carbon dioxide in the vapor phase over the temperature range from 140° to 180°C. With a rise of temperature and a consequent increase of total pressure, the vapor composition becomes richer in ammonia at any loading composition less than $L=2.28$, while it becomes richer in carbon dioxide at more than $L=2.28$.

Summary

(1) For the purpose of studying the liquid-vapor equilibria of the CO_2-NH_3-Urea-H_2O system in the presence of excess ammonia and carbon dioxide respectively over that combined as ammonium carbamate, the equilibrium pressure and vapor composition of the system under high temperature and pressure have been determined over the range of the loading NH_3-CO_2 mole ratio from 1.60 to 3.00.

(2) The experiments which were performed with an initial loading density of ammonium carbamate into a reaction vessel of 0.60 g./cc. and at a temperature of 160°C. have definitely shown the system to exert the minimum pressure and simultaneously to have the vapor composition of $2NH_3$ to $1CO_2$ at a loading mole ratio of 2.43 NH_3 to $1CO_2$.

(3) The relation between the equilibrium pressure and the mole ratio of NH_3 to CO_2 in the vapor phase has been given diagrammatically over the temperature range from 140° to 180°C.

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