Equilibrium of the CO_2-NH_3-Urea-H_2O System under High Temperature and Pressure. II. Liquid-Vapor Equilibrium in the Loading Mole Ratio of $2NH_3$ to CO_2⁽¹⁾

By Schōhachi KAWASUMI

(Received December 17, 1951)

It is an established experimental fact that the yield of urea in urea-synthesis from ammonia and carbon dioxide depends upon the loading density or ratio of the weights of the materials to the total volume of the reaction vessel at a given temperature. The writer showed in the previous paper(2) that the equilibrium pressure as well as the urea-yield is a function of the loading density at a given temperature, and explained that the diversity of the equilibrium pressure is based upon that of the equilibrium composition of the liquid and vapor phase.

The object of the present paper is to show the relations within the equilibrium composition of the liquid and vapor phase, the loading density and the temperature, by analysing the composition of the two phases under high temperature and pressure. For this purpose the vapor composition, or mole ratios of ammonia, carbon dioxide and water in the vapor-phase, the liquid composition, or mole ratio of unconverted ammonia to carbon dioxide in the liquid-phase, the converted amount to urea, and liquid-vapor volume ratio have been determined respectively by the following analytical methods in the loading mole ratio of 2 ammonia to 1 carbon dioxide.

The liquid- and vapor-phase compositions in the equilibrium state of the system have been calculated from these data. From these results the effects of the loading density and the temperature respectively on the calculated equilibrium compositions and the equilibrium constant of the following reaction have been discussed.

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

Experimental Procedure

Method of Determining the Vapor Compositions.—It is concluded that the reaction in urea-synthesis from ammonia and carbon dioxide takes place in the liquid phase, with which the vapor phase composed of CO_2, NH_3 and H_2O is in a state of equilibrium in the reaction vessel. The writer investigated the mole ratio of CO_2, NH_3 and H_2O is in a state of equilibrium in the reaction vessel. The writer investigated the mole ratio of CO_2, NH_3 and H_2O in the vapor phase by the following method.

(1). **Experimental Apparatus.**—The experimental apparatus consists of the reaction vessel (A), vapor holder (B), and gas-analyzing apparatus (C) as shown in Fig. 1. A is just the same as the apparatus used for pressure measurement reported in the previous paper(2). The vapor and liquid were kept in a state of equilibrium in the reaction vessel (A-3). The readings of equilibrium pressure by the pressure gauge (A-2) became constant after 5 to 6 hours at such a high temperature as 160°C. The gas sample was withdrawn from the vapor phase after 20 hours of being in a state of equilibrium. The vapor-holder (B) is a bottle of 3 liter capacity (B-1), which is dipped in the thermo-regulated water bath at 90°C. and provided with a mercury-dropping apparatus. A part of the vapor in A-3 which is under high temperature and pressure is discharged into B-1 at the state of 90°C. and 1 atm. The gas-analyzing apparatus (C) consists of a washing bottle of 1 normal sulphuric acid aqueous solution (C-1), which is kept in the thermostat at 70°C., U-tubes with calcium chloride (C-2 and C-4) and kali-bulb (C-3). The mole ratio of CO_2, NH_3 and H_2O in the vapor was analyzed, sending the vapor in B-1 through this apparatus (C) gradually.

(2). **Procedure of Vapor Sampling.**—After heating the reaction vessel at a given temperature for 20 hours, the vapor in a state of equilibrium with the liquid was gently withdrawn through a 4 mm. high pressure valve (A-1) into a previously evacuated vapor-holder (B-1), which had been kept at the constant temperature of 90°C. to avoid the condensation of ammonium carbamate. To keep the condition of equilibrium between the vapor and the liquid in A-3, the valve (A-1) was adjusted by the reading of mercury head in a closed mercury manometer (B-6).

The sampling procedure through the valve (A-1) as described above—a method to get a gas sample at 90°C. and at the ordinary pressure—is the most

---

(1) A part of this paper was presented at the annual meeting of the Chemical Society of Japan held at Tokyo, on 6 April 1951.

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

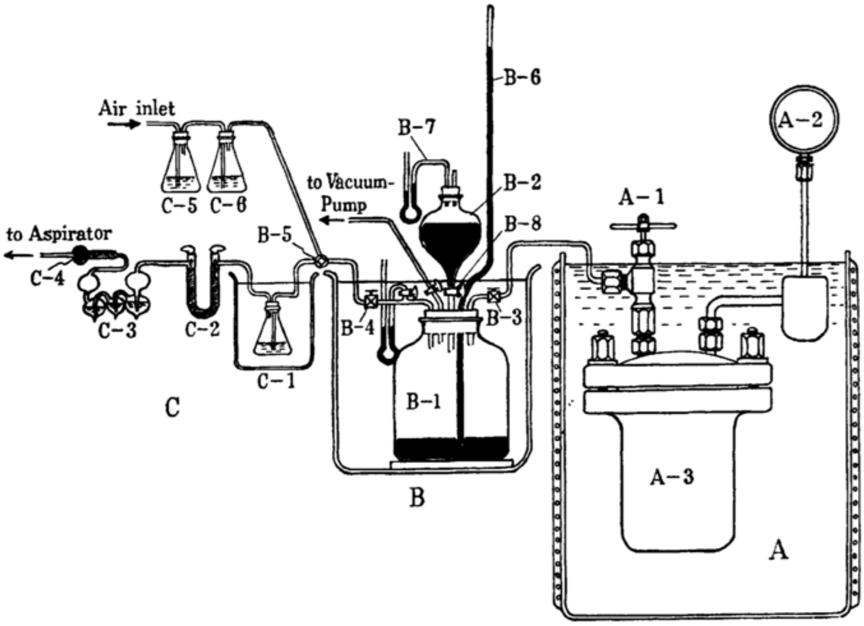


Fig. 1. –Apparatus for measuring the vapor compositions.

important. When the pressure of B-1 reached about 760 mmHg, the valve (A-1) and a screw-cock (B-3) were closed. At the temperature of 160°C. and the equilibrium pressure 70 to 150 kg./cm.^{2}, the readings of pressure drop were constantly between 5 and 7 kg./cm^2. The pipe between A-1 and B-3 which is exposed in the air, was heated to more than 70°C. by gas heating in order to avoid the condensation of the ammonium carbamate while withdrawing the vapor.

(3). **Determination of Mole Ratios of CO_2, NH_3 and H_2O.**—After the vapor was withdrawn, the vapor in B-1 was sent into an analyzing apparatus (C) at the constant velocity by dropping mercury in B-2 into B-1. The dropping velocity of mercury was regulated by a cock (B-8) according to pressure difference of a manometer (B-7). The dropping rate of mercury at each time was regulated on the average to about 40 cc. per minute. Ammonia was absorbed in C-1, water vapor in C-2 and C-4, and carbon dioxide in C-3. After the mercury-dropping procedure was finished, ammonia, carbon dioxide and water vapor in the dead space of C were completely driven into the absorbers by sending air which was introduced after being washed by concentrated KOH solution (C-5) and H_2SO_4 solution (C-6), by manipulating a three-way cock (B-5).

After the gas-absorbing procedure was finished, the four apparatuses C-1, C-2, C-3 and C-4 were weighed to obtain their increments. The increments of the kali-bulb (C-3) is the amount of carbon dioxide absorbed. And the amount of ammonia absorbed was found by titrating the solution in C-1 with 1-N NaOH solution. The amount of water vapor absorbed in C is the difference between the sum of the increments of both C-1 and C-2 and the absorbed amount of ammonia. In one gas-sampling procedure, the average value of the gas-analysis of two or three times was taken by dividing the sample in B-1 into two or three parts.

C-1 was kept at the constant temperature of 70°C. to minimize the absorption or solution of carbon dioxide into the dilute H_2SO_4 solution (C-1). The writer examined the analytical error which happened by the absorption or solution of carbon dioxide in the preliminary experiment, in which C-1 was kept over the temperature range 10 to 80°C. The amount of carbon dioxide absorbed in the kali-bulb (C-3) was measured by sending the decomposition gas which had been generated by heating 0.50 g. (0.00641 Mole) of ammonium carbamate, into the apparatus (C). The amount of N/2 H_2SO_4 solution in C-1 was 130 cc. The experimental results showed that the temperature of C-1 has to be kept at 70 to 80°C. by all means.

(4) **Accuracy of analysis.**—The above-mentioned analysis requires skill in the procedure, especially in the quantitative analysis of water vapor, or else the error becomes larger. It was confirmed by analyzing samples of known composition that the experimental error of this analytical procedure was less than 1 % in ammonia, but about 3 to 5 % in carbon dioxide and water vapor respectively. Obviously in most cases, carbon dioxide shows a tendency to negative error and water vapor to positive error.

Method of Determining Liquid Compositions.—A liquid sample which had been withdrawn from the equilibrium vessel under high temperature and pressure was analyzed by the following procedure to study the mole ratio of the unconverted ammonia to carbon dioxide in it.

(1). **Experimental Apparatus.**—The experimental apparatus consists of the equilibrium vessel of the urea-synthesis reaction (A) and of the apparatus of withdrawing the liquid sample (B) as given in Fig. 2. A is just the same as the apparatus used for the pressure measurement described in the previous paper⁽²⁾, with the exception that the cover of the equilibrium vessel is fitted with a lead pipe (A-2) of inner diameter 3 mm., outer diameter 10 mm. and length 12 cm. to discharge the liquid through the high pressure valve (A-1). B-1 is a high pressure vessel of capacity 56 cc. made of stainless steel and provided with two high pressure valves (B-2 and B-3), employed for introducing and withdrawing the liquid sample respectively, since the liquid discharged into B-1 exerts more than atmospheric pressure even at the ordinary temperature.

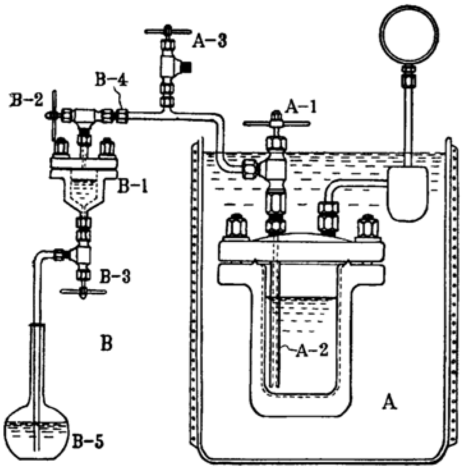


Fig. 2.—Apparatus for measuring the liquid compositions.

(2) **Procedure of Sampling.**—The procedure of withdrawing the liquid sample is more difficult than that of the sampling of vapor. The least analysable quantity of the liquid sample must be withdrawn without disturbing the liquid-vapor equilibrium by the opening of the valve (A-1), and it must be accomplished as quickly as possible, since a slow manipulation will bring about the vaporisation of the liquid through the valve (A-1). Moreover, the liquid in B-1 at the ordinary temperature is solidified too readily to be discharged from B-1. But these difficulties were nearly overcome by the following method. After the contents of the reaction vessel (A) had arrived at a condition of equilibrium at a given temperature, a very small liquid sample was expelled through the two valves (A-1 and A-3), and then the liquid was driven into B-1 through the two valves (A-1 and B-2) and the steel pipe between A-1 and B-2. This steel pipe had previously been heated at 80 to 100°C. by gas heating. A suitable amount of water had previously been charged in B-1 in order to prevent the solidification of the liquid sample. The amount of the liquid sample could be regulated by the amount of water in B-1. Under a condition of the equilibrium vessel at 160°C. and 90 kg./cm^2., for example, the pressure falls to 85 kg./cm^2. by the withdrawal of the liquid sample, but recovers and rises again after a while. After B had been separated from A by disconnecting the nut (B-4), B-1 was intensely shaken to make the contents in it homogeneous, and then by opening the valve (B-3) gently, the aqueous solution in B-1 was discharged into a measuring flask (B-5) of capacity 500 cc., in which some water had previously been charged to catch even a small amount of the vapor from the solution. By pouring the washing water into B-1 through the valve (B-2), the sample in B-1 was completely washed out to make the total amount of the sample 500 cc.

(3). **Determination of the Mole Ratio of Ammonia to Carbon Dioxide.**—The mole ratio of ammonia to carbon dioxide in the aqueous solution withdrawn by such a method as stated above was determined by the following method. An aliquot portion (50 cc.) of the sample 500 cc. was taken for determination of the unconverted ammonia by titration with 1-N sulphuric acid. Unconverted carbon dioxide in the sample was analyzed in an apparatus as shown in Fig. 3. The other aliquot portion (50 cc.) was taken into a bottle (C-1), together with a few drops of methylorange as the indicator. Carbon dioxide generated by dropping concentrated sulphuric acid from a funnel (C-3) after the bottle (C-1) was immersed into a thermostat (C-2) at 70°C., was absorbed in potassium hydroxide solution (C-7) through a U-tube with calcium chloride (C-6). The dropping of sulphuric acid was continued until the color of the indicator in C-1 changed. After the generation of carbon dioxide had ended, carbon dioxide in the dead space was completely made to absorb in C-7 by sending air refined through concentrated potassium hydroxide solution (C-4) and sulphuric acid (C-5) by means of an aspirator. The increment of kali-bulb (C-7) is equal to the amount of carbon dioxide absorbed. Each sample was analyzed three times and the mean value was taken.

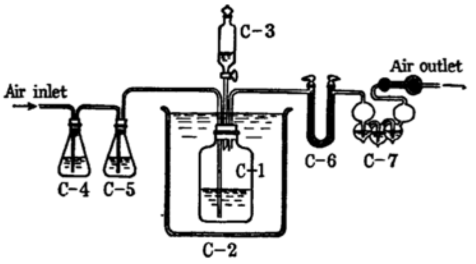


Fig. 3.—Apparatus for determination of carbon dioxide.

(4). **Accuracy of Analysis.**—At the above method of analysis, though the excess addition of sulphuric acid for the generation of carbon dioxide after the neutralisation was reached, should result in a hydrolysis of urea and a consequent increase in the analytical value of carbon dioxide, an experiment showed that even when 50 cc. more sulphuric acid than necessary for the neutralisation was used, the value of carbon dioxide was only 0.15 % higher than theoretical. Therefore, it has become evident that the above method is not made invalid by the reaction of urea-decomposition.

Experimental Results

Relation between Vapor Composition and Loading Density.—As mentioned in detail in the previous paper⁽²⁾, the equilibrium pressure of the urea-synthesis reaction greatly depends upon the loading density, that is to say, the former increases with the latter at a given temperature under a condition in which the loading mole ratio of carbon dioxide to ammonia is one by two. It is an important problem to clear up how the vapor composition depends upon the loading density in this case. The writer studied the relation between the vapor composition and the loading density at 160°C.

The experimental results showed that the mole ratio of ammonia to carbon dioxide in the vapor is less than two at each loading density, and the more loading density increases, the richer the carbon dioxide in the vapor composition becomes, as shown in Fig. 4. Therefore, it is clear that the equilibrium pressure increases with the loading density, as the increase of the loading density accompanies at the same time the increase of carbon dioxide content in the vapor phase. These experimental results are based on the fact that the solubility of ammonia into the liquid phase is more than that of carbon dioxide. Moreover, the experimental results showed that the measured mole ratio of water to carbon dioxide in the vapor,—though there exists a very small quantity of water vapor—, is nearly within the range of 0.03 to 0.16.

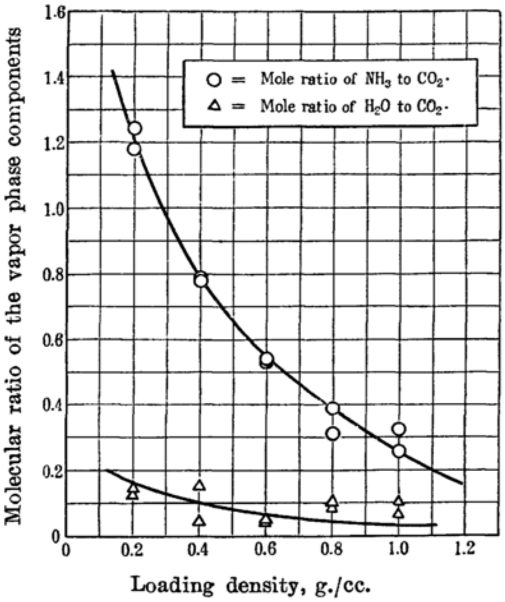


Fig. 4.—Relation between the vapor composition and the loading density at 160°C.

Relation between Vapor Composition and Temperature.—The equilibrium pressure rises with temperature at a constant loading density as explained in the previous paper.⁽²⁾ At the same time, it is expected in this case that the vapor composition undergoes a change with the change in temperature. The result of the experiments in which the vapor composition was measured at the loading density 0.60 g./cc. and over the temperature range of 140 to 180°C., is shown in Fig. 5. The observed mole ratio of ammonia to carbon dioxide ranges from 0.47 to 0.65 under this condition and the vapor composition becomes richer in ammonia with the rise of temperature. The relation between the mole ratio of carbon dioxide to ammonia and temperature is nearly linear within the range of the experiments. Mole ratio of water to carbon dioxide ranges from 0.02 to 0.12.

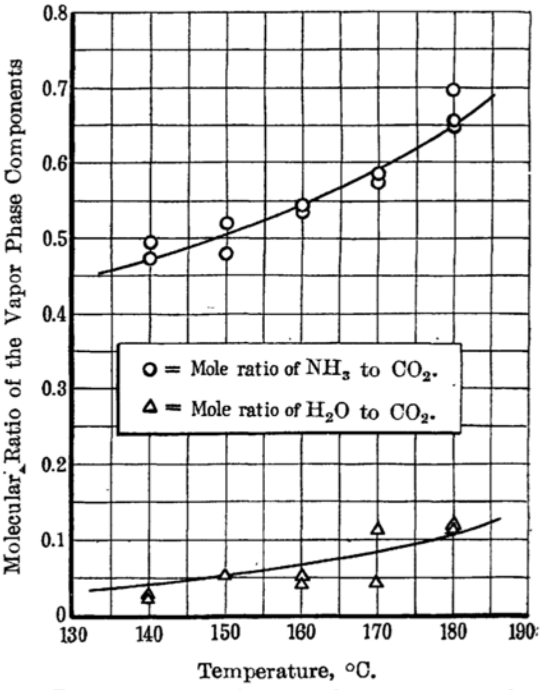


Fig. 5.—Relation between the vapor composition and the temperature at a loading density of 0.60 g./cc.

Relation between Liquid Composition and Loading Density.—The effect of the variation of

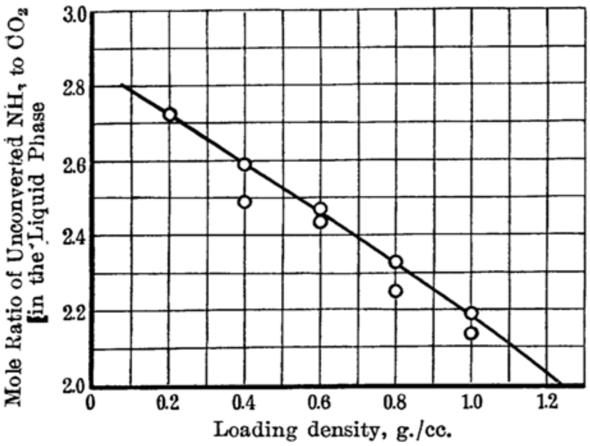


Fig. 6.—Relation between the liquid composition and the loading density at 160°C.

the loading density on the mole ratio of ammonia to carbon dioxide in the liquid phase which is in equilibrium with the vapor was studied at 160°C. and the loading densities of 0.20 to 1.00 g./cc. The experimental results are shown in Fig. 6. The mole ratio of ammonia to carbon dioxide increases from 2.18 to 2.72 within the range of the experiments; thus the liquid composition becomes richer in ammonia, with decrease of the loading density. This is closely connected with the facts that the vapor composition becomes richer in ammonia as described above and the yield of urea decreases, with decrease of the loading density. The point where the curve intersects the abscissa in Fig. 6 is nothing but the loading density where the mole ratio of ammonia to carbon dioxide in the liquid phase becomes equal to the loading mole ratio, or where the equilibrium vessel is filled up with only the liquid phase. This loading density is 1.24 g. per cc., being consistent with the maximum loading density which will be derived from the relation between the ratio of liquid volume to vessel volume and the loading density in the following section of this paper.

Relation between Liquid Composition and Temperature.—The effect of the change in temperature on the mole ratio of ammonia to carbon dioxide in the liquid phase was studied at the loading density 0.60 g./cc. and over the temperature range of 140 to 180°C. The experimental results are shown in Fig. 7. The mole ratio of unconverted ammonia to carbon dioxide increases from 2.26 to 2.67 within the range of the experiments; thus the liquid composition becomes richer in ammonia, with the rise of temperature. The mole ratio in the liquid composition is approximately a linear function of the temperature as shown in Fig. 7. This line intersects the abscissa at about 115°C. and this point is nothing but the temperature where the mole ratio of ammonia to carbon dioxide in the liquid phase becomes equal to the loading mole ratio, or the transition temperature, where the content in the equilibrium vessel undergoes a change from the solid- to the liquid-phase reaction. This transition temperature has been fully investigated by Kitawaki, Hori and Shimoda.⁽³⁾ According to their investigations, a junction of the decomposition pressure-temperature curve of solid ammonium carbamate and the equilibrium pressure-temperature curve of the mixed solution of the CO_2-NH_3-Urea-H_2O system was 114.6°C., being consistent with the transition temperature from the solid- to the liquid-phase reaction, where a discontinuous point appears, in a plot of the yield of urea against the temperature, as shown in Fig. 8.

Relation among Urea-Yield, Loading Density and Temperature.—Fichter and Becker⁽⁴⁾ discovered in 1911 that the equilibrium yield of urea increaes with the loading density at a given temperature. Thereafter, the effect of the loading density on the equilibrium yield of urea was studied by Clark, Gaddy and Rist,⁽⁵⁾ and M. Tokuoka,⁽⁶⁾ the former specially studied the effect at such a higher loading density as 1.0 g./cc. over the temperature range of 135 to 200°C. The writer also studied the relation between the equilibrium yield of urea

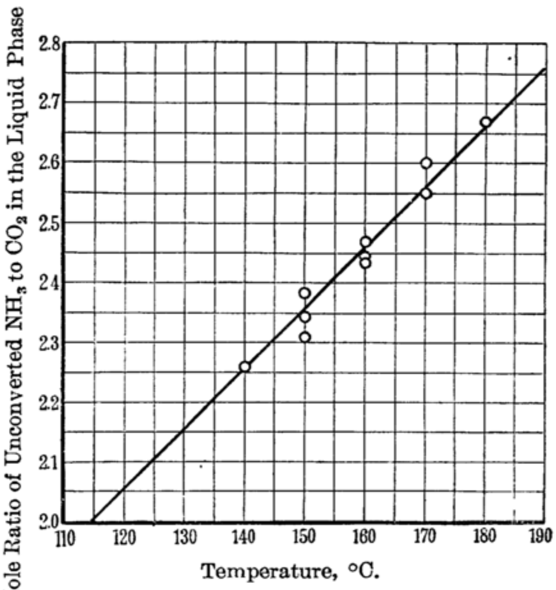


Fig. 7.—Relation between the liquid composition and the temperature at a loading density of 0.60 g./cc.

---

(3) Kitawaki, Hori and Shimoda, *Bull. Gov. Chem. Ind. Res. Inst. Tokyo*, **32**, No. 6 and 10 (1937).

(4) Fichter and Becker, *Ber.*, **44**, 3473 (1911).

(5) Clark, Gaddy and Rist, *Ind. Eng. Chem.*, **25**, 1092 (1933).

(6) M. Tokuoka, *J. Agr. Chem. Soc. Japan*, **10**, 1333 (1934); *ibid.*, **11**, 107 (1935); *ibid.*, **11**, 174 (1935).

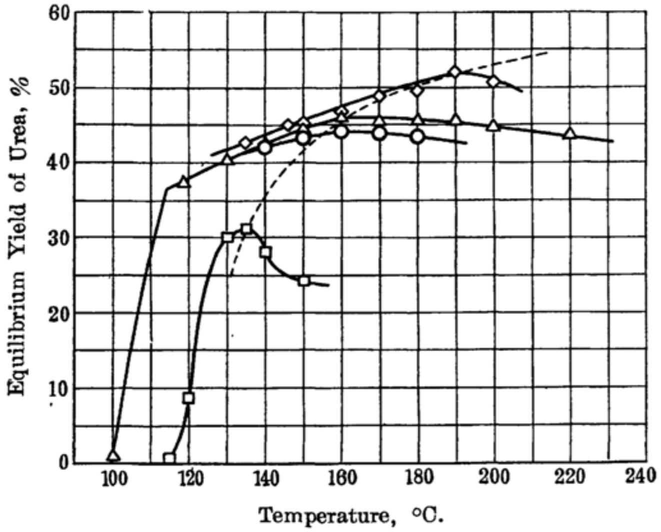


Fig. 8.—Relation between the yield of urea and the temperature.

Symbol	Loading density, g./cc.	Investigator
◇	1.00	Clark, Gaddy and Rist(5)
△	0.65	Kitawaki, Hori and Shimoda(3)
○	0.60	Present Measurement
□	0.11	Fichter and Becker(4)

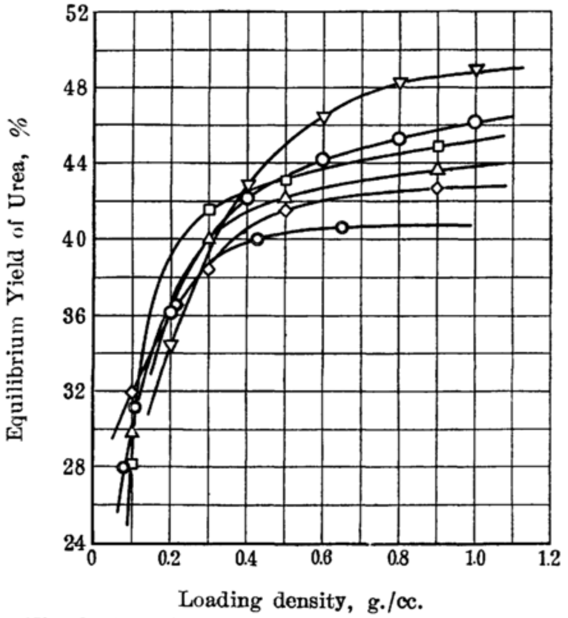


Fig. 9.—Relation between the yield of urea and the loading density.

Symbol	Temp. °C.	Investigator
▽	170	Clark, Gaddy and Rist(5)
○	160	Present Measurement
□	150	M. Tokuoka(6)
△	145	
◇	140	
◎	135	Fichter and Becker(4)

and the loading density at 160°C., in order to calculate the liquid- and the vapor-phase compositions in a state of equilibrium. Experimental results showed that the average yields of urea are 36.2, 42.2, 44.2, 45.3, and 46.2 % at the loading densities 0.20, 0.40, 0.60, 0.80, and 1.0 g./cc., respectively. The data cited above are shown graphically in Fig. 9.

In general it had been thought that the yield of urea increases with the rise of temperature at a given loading density, but Fichter, and Becker(4) showed that the yield of urea at a loading density of 0.11 g./cc. attains to the maximum at 135°C. Thereafter, the maximum yields of urea were experimentally shown at about 160°C. and 0.65 g./cc. by Kitawaki, Hori and Shimoda,(3) and at about 190°C. and 1.0 g./cc. by Clark, Gaddy and Rist,(5) respectively, as given in Fig. 8. The writer also studied the effect of the temperature on the equilibrium yield of urea at a loading density of 0.60 g./cc. Experimental results showed that the average yields of urea are 42.1, 43.3, 44.2, 44.0, and 43.5 % at 140°, 150°, 160°, 170°, and 180°C., respectively. Clark and others(5) explained that the lower yield of urea obtained above 190°C. may be attributed to the complications introduced by the more active corrosion of the reactor and to the increased tendency for the thermal dissociation of urea and the catalytic cracking of ammonia. However, the reason why these experiments showed increasing conversion of ammonium carbamate into urea with temperature up to the maximum at a given loading density, must essentially be attributed to the inevitable relations among the urea-yield, the loading density and the temperature, which result from the liquid- and the vapor-phase equilibrium of the CO_2-NH_3-Urea-H_2O system. Evidently, according to the data cited above, the temperatures where the equilibrium yield of urea attains to the maximum, rise with the increase of the loading density, drawing such a locus as a dotted line shown in Fig. 8.

In Fig. 10 which is a schematic expression of Fig. 9, it can readily be understood that the urea-yield Y_1 at the temperature T_1 is less than Y_2 at the lower temperature

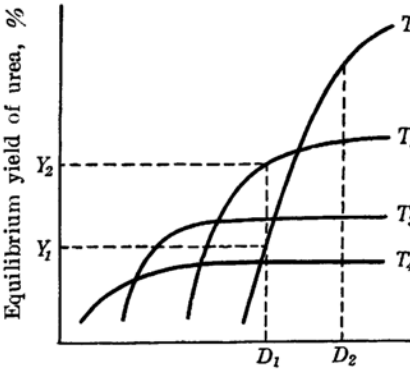
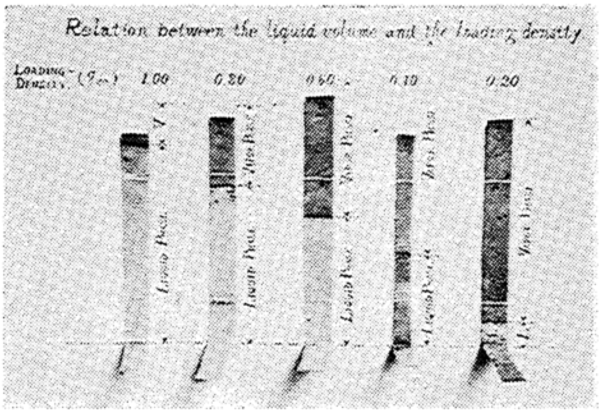


Fig. 10.—Schematic diagram of relation among the yield of urea, the loading density and the temperature.

T_2, and Y_2 is the maximum urea-yield at a given loading density of D_1. Therefore we must raise the temperature and increase the loading density at the same time in order to increase the yield of urea. It is because of the decrease of vapor-phase volume, or of the incrase of ratio of the liquid-phase weight to the initial loading weight, that the yields of urea increase, with the increase of the loading density at a given temperature, as pointed out by Matignon and Fréjacques.(7) Krase and Gaddy(8) have also explained that since the equilibrium is established in the liquid phase and presumably only a negligible amount, if any, of urea is in the gaseous phase, the extent of conversion of carbamate to urea is dependent on the ratio of the volumes of liquid and gas phases. Similarly the existence of the maximum yield of urea in a plot of the yield against the temperature at a given loading density is attributable to the circumstances; while the conversion of ammonium carbamate to urea in the liquid phase increases, the quantity of liquid phase itself decreases with the rise of temperature. Ultimately the reason why such relations as shown in Fig. 10 arise among the urea-yield, the loading density and the temperature, must be accounted for by the fact that the equilibrium yields of urea depend not only upon the equilibrium of the reaction of urea-synthesis in the liquid-phase, but also upon the liquid- and vapor-phase equilibrium.

Volume-Ratio of Vapor- to Liquid-Phase.—As the equilibrium state between the vapor and liquid in an autoclave under high temperature and pressure is difficult to survey with the naked eyes, the writer tried to measure the volume-ratio of the vapor to the liquid by the following method in order to calculate the vapor- and liquid-density.

Photo. 1



In the urea-synthesis reaction from ammonia and carbon dioxide, the corrosive action of the reacting system for the materials of the reaction vessel is so violent, that there appears a distinct corrosive line on the material which corresponds to the boundary of the two phases. Aluminium or 18Cr-8Ni stainless steel of about 20 cm. long, 15 mm. wide and 1 to 2 mm. thick, was bent at right angles as shown in Photo. 1 and inserted into the reaction vessel so that the plate might not move in it. After heating the reaction vessel at a given temperature for about 20 hours, the plate was taken out from the vessel. As shown in Photo. 1, a part of the plate which was dipped in the molten reaction mixture suffered more corrosive action and grew thinner than the other part exposed in the vapor; especially at the boundary of the two phases it suffered a violent corrosion. We can readily determine the volume-ratio of the two phases with about ±1 % error

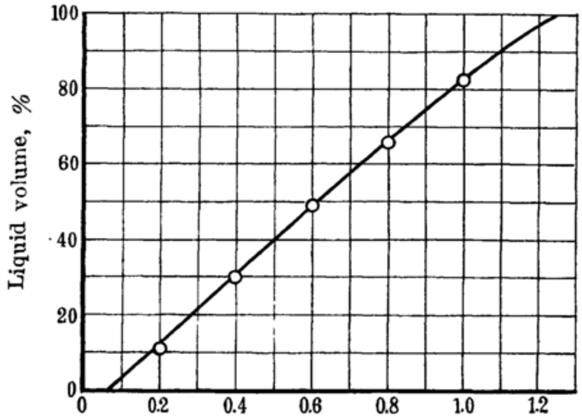


Fig. 11.—Relation between liquid volume and loading density at 160°C.

---

(7) Matignon and Fréjacques, *Bull. soc. chim.*, **31**, 394 (1922).

(8) Krase and Gaddy, *Ind. Eng. Chem.*, **14**, 611 (1922).

from the plate. The volume of the autoclave is about 750 cc. The data from these experiments concerning the percentage of liquid volume to vessel volume at 160°C. and over the loading density range of 0.2 to 1.0 g./cc., is given in Fig. 11 and Photo. 1. The loading density, in which the liquid volume to the total volume of the autoclave is 100 %, is nothing but the liquid density in the case of the autoclave filled up with the liquid. It will be sought by the extrapolation from Fig. 11 that the maximum loading density is about 1.24 g./cc. at 160°C. which is in good agreement with that which was derived from the relation between the mole ratio of unconverted ammonia to carbon dioxide in the liquid phase and the loading density.

The experimental results on the percentage of liquid volume to vessel volume at the loading density 0.60 g./cc. and over the temperature range of 140 to 180°C. is given in Table 1. The experiments showed that the percentage of liquid volume is nearly constant and independent of the temperature at a given loading density within the experimental error.

Table 1

Relation between Liquid Volume and Temperature at a Loading Density of 0.60 g./cc.

Temp., °C.	Equilibrium pressure, atm.	Leiquid volume to the vessel volume, %
140	52	48.2
150	67	47.1
160	88	48.8
170	115	48.5
180	149	47.5

Discussion of Results

Relation between Equilibrium Composition and Loading Density.—For the purpose of calculating the equilibrium compositions, it is assumed that the system consists of three components, ammonia, carbon dioxide and water, in the vapor phase and of four components, urea, water, unconverted ammonia and carbon dioxide, in the liquid phase, or that there exists neither gaseous- nor melted-ammonium carbamate in the two phases under high temperature and pressure, since it is impossible to measure the amount of ammonium carbamate distinguished from unconverted ammonia or carbon dioxide, although much amount of ammonium carbamate must exist in the liquid phase. In such a case that "c" gram moles of ammonium carbamate (equivalent of "$2c$" moles of ammonia and "c" moles of carbon dioxide) were initially loaded into a reaction vessel of 1 litre volume, we obtain from the material balance respectively;

$$n_{\text{urea}}+n_{\text{CO}_2}+n'_{\text{CO}_2}=c \tag{2}$$

$$2n_{\text{urea}}+n_{\text{NH}_3}+n'_{\text{NH}_3}=2c. \tag{3}$$

Let us put,

$$n'_{\text{NH}_3}/n'_{\text{CO}_2}=R' \tag{4}$$

$$n'_{\text{H}_2\text{O}}/n'_{\text{CO}_2}=S' \tag{5}$$

$$n_{\text{NH}_3}/n_{\text{CO}_2}=R \tag{6}$$

$$n_{\text{urea}}=cY \tag{7}$$

and

$$n_{\text{H}_2\text{O}}=n_{\text{urea}}-n'_{\text{H}_2\text{O}}. \tag{8}$$

From these seven equations (2) to (8), we can derive the following relations (9) to (14) which allow the equilibrium concentration of each component to be calculated.

$$n'_{\text{CO}_2}=\frac{c(1-Y)(R-2)}{R-R'} \tag{9}$$

$$n'_{\text{NH}_3}=\frac{cR'(1-Y)(R-2)}{R-R'} \tag{10}$$

$$n'_{\text{H}_2\text{O}}=\frac{cS'(1-Y)(R-2)}{R-R'} \tag{11}$$

$$n_{\text{CO}_2}=\frac{c(1-Y)(2-R')}{R-R'} \tag{12}$$

$$n_{\text{NH}_3}=\frac{cR(1-Y)(2-R')}{R-R'} \tag{13}$$

$$n_{\text{urea}}=cY \tag{7'}$$

$$n_{\text{H}_2\text{O}}=c\left\{Y-\frac{S'(1-Y)(R-2)}{R-R'}\right\}. \tag{14}$$

The compositions of the liquid- and vapor phase in the equilibrium state at a temperature of 160°C. and over the loading density range of 0.20 to 1.0 g./cc. are shown in Table 2. The equilibrium constants (K_{N_1}) of the reaction (1) represented by mole fraction (N_i) of each component in the liquid phase $K_{\text{N}_1}=\frac{N_{\text{urea}}N_{\text{H}_2\text{O}}}{N_{\text{CO}_2}N^2_{\text{NH}_3}}$ are also given in the last line of Table 2. These values of the equilibrium constant at 160°C. are approximately constant, independent of the loading density. A plot of mole fraction x_i of each component in two phases against the loading density is drawn in Fig 12. It is conjectured from Fig. 12 that the equilibrium yields of urea increase at a given temperature because the vapor-phase decreases or the boundary surface between the two phases rises up in the reaction vessel, with increasing loading density.

Effect of Loading Density on Liquid- and Vapor-Density.—The liquid- and vapor-density of the system under high temperature and pressure are given by dividing the weight

Table 2

Effect of Loading Density on Liquid- and Vapor-Phase Compositions in Equilibrium State at 160°C.

	D, g./cc.	0.20	0.40	0.60	0.80	1.00
	c, mole/l.	2.562	5.123	7.685	10.247	12.808
	P, atm.	69	76.5	89	107.5	136.5
	R'	1.347	0.816	0.547	0.405	0.325
	S'	0.164	0.103	0.066	0.045	0.033
	R	2.725	2.590	2.460	2.326	2.180
	Y	0.362	0.422	0.442	0.453	0.462
Equilibrium Concentration, mole/l.	n'_{CO_2}	0.859	0.984	1.031	0.951	0.669
	n'_{NH_3}	1.158	0.803	0.564	0.385	0.217
	n'_{H_2O}	0.141	0.102	0.068	0.043	0.022
	n_{CO_2}	0.774	1.975	3.257	4.654	6.222
	n_{NH_3}	2.109	5.115	8.012	10.823	13.563
	n_{urea}	0.928	2.164	3.397	4.642	5.918
	n_{H_2O}	0.787	2.063	3.329	4.599	5.895
Equilibrium mole fraction	N'_{CO_2}	0.398	0.521	0.620	0.690	0.737
	N'_{NH_3}	0.537	0.425	0.339	0.279	0.239
	N'_{H_2O}	0.065	0.054	0.041	0.031	0.024
	N_{CO_2}	0.168	0.175	0.181	0.188	0.197
	N_{NH_3}	0.459	0.452	0.445	0.438	0.429
	N_{urea}	0.202	0.191	0.189	0.188	0.187
	N_{H_2O}	0.171	0.182	0.185	0.186	0.187
	K_{N_1}	0.976	0.977	0.974	0.968	0.963

of each phase obtained from Table 2 by the liquid- and vapor-volume respectively. The densities (d and d') of the two phases at 160°C. and over the loading density range 0.20 to 1.00 g./cc. increase with the loading density as shown in Fig. 13. The extrapolation of the liquid-density curve in Fig. 13 shows that the liquid density at the maximum loading density of 1.24 g./cc. is identical with the latter. The vapor density (d') is approximately a linear function of the equilibrium pressure as shown in Fig. 14.

Relation between Equilibrium Composition and Temperature.—The results of calculation of the liquid- and vapor-phase compositions in the equilibrium state at a loading density of 0.60 g./cc. and over the temperature range of 140 to 180°C. are shown in Table 3. A plot of mole fraction x_i against the temperature is shown in Fig. 15. It is conjectured from Fig. 15 that the maximum yield of urea in a plot of the yield against the temperature

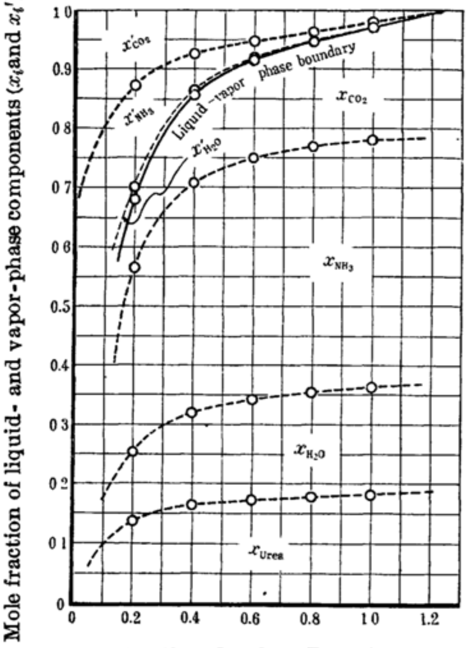


Fig. 12.—Liquid-vapor equilibria diagram of the CO_2-NH_3-Urea-H_2O system at a temperature of 160°C.

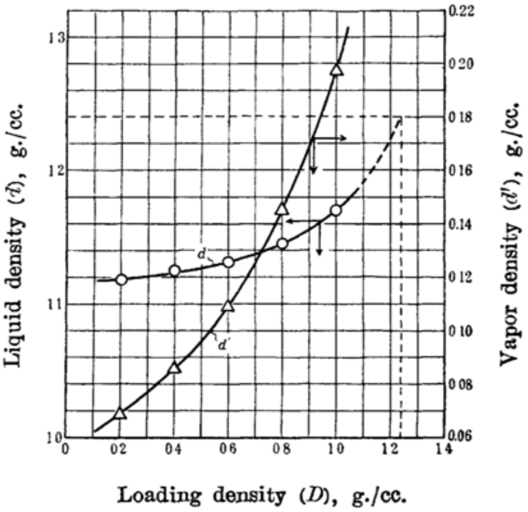


Fig. 13.—Effect of loading density on liquid- and vapor-density at 160°C.

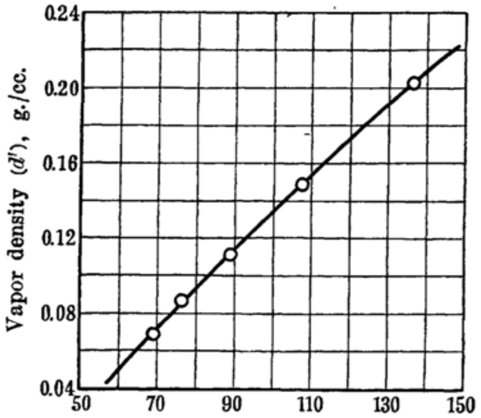


Fig. 14.—Relation between vapor density and equilibrium pressure at 160°C.

Table 3

Effect of Temperature on Liquid- and Vapor-Phase Compositions in Equilibrium State at a Loading Density of 0.60 g./cc.

	Temp., °C.	140	150	160	170	180
	c, mole/l.	7.685	7.685	7.685	7.685	7.685
	P, atm.	50.5	68	89	117	151
	R'	0.470	0.505	0.545	0.592	0.650
	S'	0.040	0.052	0.066	0.082	0.105
	R	2.260	2.360	2.460	2.562	2.665
	Y	0.421	0.433	0.442	0.440	0.435
Equilibrium Concentration, mole/l.	n'_{CO_2}	0.646	0.845	1.031	1.227	1.432
	n'_{NH_3}	0.303	0.427	0.564	0.726	0.931
	n'_{H_2O}	0.026	0.044	0.068	0.100	0.150
	n_{CO_2}	3.803	3.512	3.257	3.076	2.910
	n_{NH_3}	8.590	8.290	8.012	7.880	7.760
	n_{urea}	3.235	3.327	3.397	3.381	3.343
	n_{H_2O}	3.209	3.283	3.329	3.281	3.193
Equilibrium Concentration, mole fraction	N'_{CO_2}	0.662	0.642	0.620	0.597	0.570
	N'_{NH_3}	0.311	0.324	0.339	0.354	0.370
	N'_{H_2O}	0.027	0.034	0.041	0.049	0.060
	N_{CO_2}	0.202	0.190	0.181	0.174	0.169
	N_{NH_3}	0.456	0.451	0.445	0.448	0.452
	N_{urea}	0.172	0.181	0.189	0.192	0.194
	N_{H_2O}	0.170	0.178	0.185	0.186	0.185
	K_{N_1}	0.697	0.833	0.974	1.021	1.046

at a given loading density is based on the fact that the vapor-phase increases with the rise of temperature. The equilibrium constants K_{N_1} of the reaction (1) represented by mole fraction N_i are shown in the last line of Table 3. There appears a discontinuous point at 160°C. in a plot of the equilibrium constant against the temperature. Hori and Ogami [9] have already found that a plot of the logarithm of the equilibrium constant[(10)] against the reciprocal of the temperature results in two straight lines intersecting at 154°C. This conclusion was reached in their experiment which was effected at a loading density of 0.65 g./cc. in a reaction vessel of sealed glass tube, and explained that the existence of the discontinuous point may possibly be based on the difference between the phases in the equilibrium state of the system at each temperature, that is to say, between the solid- and vapor-phase equilibrium at lower temperature than 154°C. and the liquid- and vapor-phase equilibrium at higher temperature than 154°C., because this point perfectly coincides with the melting point 153.5 to 155.8°C. of ammonium carbamate observed by Kitawaki, Hori and Shimoda[(3)]. The other values of the melting point of ammonium carbamate which were reported by Terres and Behrens[(11)], E. Jänecke[(12)], and Krase, Gaddy and Clark[(13)] are 147 to 150°C.,

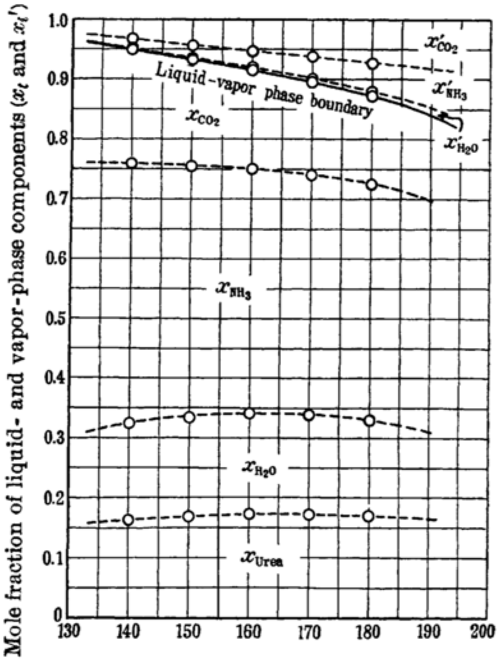


Fig. 15.—Liquid-vapor equilibria diagram of the CO_2-NH_3-Urea-H_2O system at a loading density of 0.60 g./cc.

---

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

(10) The equilibrium constant employed by Hori and Ogami was represented by mole fraction derived from the initial loading composition and the yield of urea without distinction between the liquid- and the vapor-compositions.

(11) Terres and Behrens, *Z. physik. Chem.*, **139 A**, 695 (1928).

(12) E. Jänecke, *Z. Elektrochem.*, **35**, 716 (1929).

(13) Krase, Gaddy and Clark, *Ind. Eng. Chem.*, **22**, 289 (1930).

153 and 145°C. respectively.

The fusion of ammonium carbamate, however, is a complicated phenomenon connected inevitably with the formation of equi-molar urea and water, as pointed out by Kitawaki and others,(3) because its melting point depends on the rate of heating carbamate and in cooling the molten ammonium carbamate, in which even a small quantity of urea was always detected, it is not solidified at the temperature where pure solid carbamate itself began to melt in heating it. In other words, the respective temperature observed in such a way is only an apparent melting point of carbamate, which may possibly depend upon the initial loading density of carbamate in a vessel. Since the equilibrium system, which is the subject under consideration, is a homogeneous liquid phase at a higher temperature than the transition point 115°C., the explanation that the discontinuous point corresponds to the melting point of ammonium carbamate is unreasonable. Preferably it ought to be considered that the discontinuous point corresponds to the maximum yield of urea in Fig. 8 and consequently varies depending on the initial loading density of carbamate.

This unaccountable relation between the equilibrium constant and the temperature might result from the inadequate initial assumption that the system consists of four components of urea, water, ammonia and carbon dioxide in the liquid phase. In other words, it seems to be impossible to represent the reaction of the urea formation by such a simple reaction as the equation (1). Therefore, for the complete explanation of the relation, further consideration should be tried from other stand-points and on other assumptions.

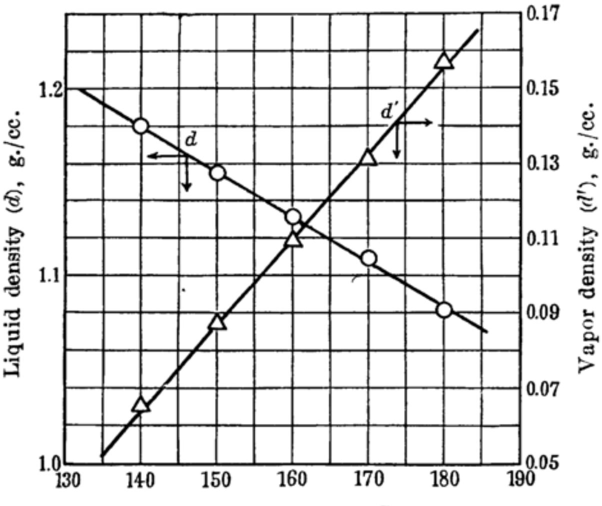


Fig. 16.—Effect of temperature on liquid- and vapor-density at a loading density of 0.60 g./cc.

Effect of Temperature on Liquid- and Vapor-Density.—From the weight of each phase obtained from Table 3 and the volume of each phase, the liquid- and vapor-density at a loading density of 0.60 g./cc. and over the temperature range of 140 to 180°C. has been calculated as shown in Fig. 16. The liquid-density decreases and the vapor-density increases linearly with the rise of temperature, respectively.

Summary

(1) For studying the liquid-and vapor-phase equilibrium of the CO_2-NH_3-Urea-H_2O system under high temperature and pressure, details of methods to determine mole ratios of ammonia, carbon dioixde and water in the vapor phase, mole ratio of ammonia to carbon dioxide in the liquid phase, and volume-ratio of the vapor-to liquid-phase in an autoclave have been described.

(2) Experimental results at temperatures between 140 and 180°C. and over the loading density range of 0.20 to 1.00 g./cc. have been shown in the case of the loading mole ratio of $2NH_3$ to 1 CO_2.

(3) The relations among the equilibrium yield of urea, the loading density and the temperature were discussed from the standpoint of the liquid- and vapor-phase equilibrium.

(4) The liquid- and vapor-phase compositions in the equilibrium state of the system have been calculated on an assumption that the system consists of three components, ammonia, carbon dioxide and water, in the vapor phase and of four components, urea, water, ammonia and carbon dioxide, in the liquid phase.

(5) The equilibrium constant of the following reaction represented by mole fraction of each component in the liquid phase is approximately constant independent of the loading density at a given temperature.

$$CO_2 + 2NH_3 \rightleftarrows CO(NH_2)_2 + H_2O$$

(6) A discontinuous point appearing in a plot of the equilibrium constant against the temperature at a given loading density has been discussed.

(7) The liquid- and vapor-densities of the system under high temperature and pressure have been calculated from

the equilibrium compositions.

Nomenclature

Symbols-

c —Number of moles of ammonium carbamate loaded initially into the reaction vessel, gram mole per litre
d —Density of liquid, g. per cc.
D—Loading density, or ratio of the weights of materials to the total volume of the reaction vessel, gram per cc.
K_{N_1} —Equilibrium constant of the reaction(1) represented by mole fraction N_i, no units
n_i—Number of moles of a component "i" in the liquid phase per litre of the reaction vessel, gram mole per litre
N_i —Mole fraction of a component "i" in the liquid phase, or ratio of gram moles to the total gram moles in the liquid phase, no units
P—Equilibrium pressure, atm.
R—Mole ratio of unconverted ammonia to carbon dioxide in the liquid phase, no units
S—Mole ratio of water to carbon dioxide in the liquid phase, no units
x_i—Mole fraction of a component "i" in the liquid phase, or ratio of gram moles to the total gram moles in the two phases, no units
Y—Equilibrium yield of urea, or ratio of gram moles of urea to initial loading moles of ammonium carbamate ($= n_{\text{urea}}/c$), no units

Superscript

$'$ (dash)—sign to denote the vapor phase

The writer wishes to express appreciation for the kind guidance and the advice received throughout this work from Dr. Shinjiro Kodama, Prof. of Kyoto University, and for the encouragement received from Dr. Kenji Fujimura, the chief of the Research Department.

Research Department, Niihama Works,
Nissin Chemical Co., Ltd., Niihama