REACTION BETWEEN AMMONIA AND CARBON DIOXIDE UNDER HIGH PRESSURE.

By Ryo Kiyama and Shigeru Minomura.

Introduction.

Generally a chemical reaction under high pressure is performed in the iron vessel up to date and the reaction mechanism is explained by the changes of the pressure, volume, temperature or yield, etc. and any consideration of the mechanism contains the hypothesis.

The authors studied the reaction between ammonia and carbon dioxide in the glass vessel under the conditions of the temperature $-20\sim100^{\circ}$C, the total pressure $1\sim20$ cmHg and the temperature $50\sim200^{\circ}$C, the total pressure $1\sim300$ atm. From the inflexion of the curve of the pressure-volume-temperature relation obtained and the observation of the reaction process with the naked eye, the process of the reaction between ammonia and carbon dioxide is discussed.

Experimentals.

(1) Materials.

The preperation of ammonia : Ammonia gas is evaporated from liquid ammonia in a bomb, dried by passing through calcium oxide, kalium hydroxide and over metallic natrium, phosphorus pentoxide successively, finally distillated and presserved on phosphorus pentoxide in a flask for about a month.

The preparation of carbon dioxide : Carbon dioxide is evaporated from liquid carbon dioxide in a bomb, or prepared from heating sodium bicarbonate in a Terex tube fitted with glass wool plug to catch solid particles, dried by passing through sulphuric acid and over phosphorus pentoxide, finally distilled and preserved as in the case of ammonia.

(2) The experimental apparatus and operation at low temperature and pressure.

The experimental apparatus is shown in Fig. 1. $M_{1\sim3}$ are mercury manometers and B is a burette and the gas pressure can be controlled by M_2. V is a reaction vessel and $F_{1\sim2}$ thermostats.

The gas mixture of ammonia and carbon dioxide is led in B and the partial pressure ratio is determined by M_1 and the volume change of the gas mixture

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in B is measured at the total pressure of $1\sim20$ cmHg, at the temperatures of 0, 10, 18, 30°C and at the interval of 30 minutes. On the other hand, the gas mixture is led in V and the partial pressure ratio is determined by M_3 and the total pressure change is measured by M_3 at $-18\sim100$°C and at the interval of 30 minutes.
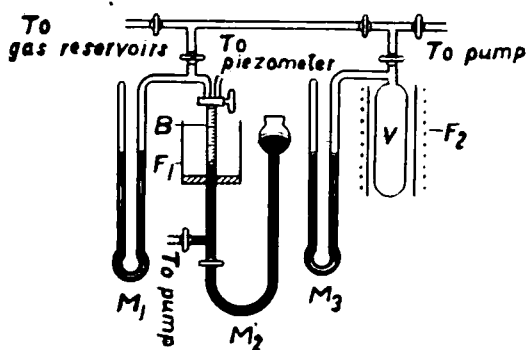

Fig. 1

(3) The experimental apparatus and operation at high temperature and pressure.

The apparatus[1] and the procedures[2] for sampling in the piezometer are the same as the reports of this Journal. The total volume of the glass piezometer is $8\sim9$ cc, in which the gas mixture of ammonia and carbon dioxide of the constant partial pressure ratio is sealed. The measured volume of the capillary of the piezometer is about 120 mm³, the inner and outer diameter are about 0.8 and 8 mm respectively. In the experiment two sets of furnace must be set on the capillary part and the bomb containing the swelling part of the piezometer, to keep a desired temperature of the reaction and to decompose ammonium carbamate perfectly before the compressing procedure begins. The total volume of the gas mixture in the measured volume of the glass capillary is measured under pressure $1\sim300$ atm at the interval of 10 minutes.

Experimental results.

(1) The reaction at low temperature and pressure.

(a) The isotherms. The pressure × volume − pressure (PV − P) curves, under the conditions of the temperature, $0\sim30$°C, the total pressure $1\sim20$ cmHg and the partial pressure ratio $NH_3 : CO_2 = 2 : 1$, are shown in Fig. 2. Every isotherm has an inflexion point and the gas mixture does not react till it reaches the point and after the point starts to react. White solid appears on the wall of the reaction vessel with increasing pressure after the point and disappears with decreasing pressure. The position of the point shifts to the high pressure at high

1) R. Kiyama and K. Suzuki, *This Journal*, 21, 50 (1951)
   R. Kiyama and K. Inoue, *ibid.*, 21, 73 (1951)
   R. Kiyama, T. Ikegami and K. Inoue, *ibid.*, 21, 58 (1951)
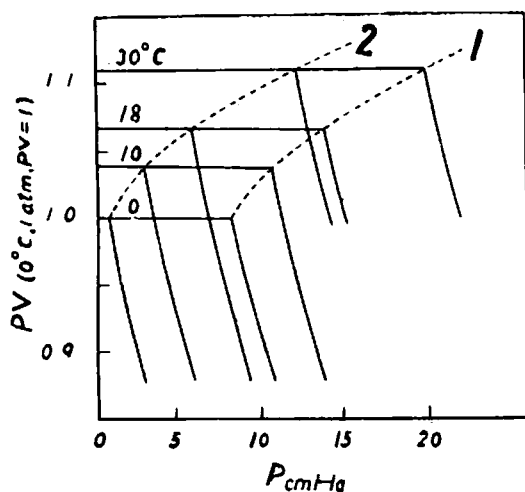2) R. Kiyama and H. Kinoshita, *ibid.*, 19, 43 (1949)

Fig. 2 $NH_3 : CO_2 = 2 : 1$. Curve 1 is the case of the mixture dried by passing through and preserving on the drying materials. Curve 2 is the case of the mixture dried only by passing through the drying materials.
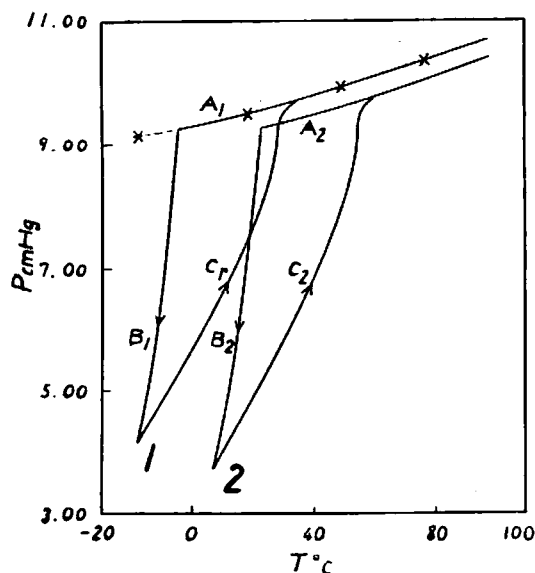
Fig. 3 $NH_3 : CO_2 = 2 : 1$. Curve 1 is the case of the mixture dried by passing through and preserving on the drying materials. Curve 2 is the case of the mixture dried only by passing through the drying materials.

temperature.

(b) **The isocores.** The reaction under the conditions of the temperature, $-20 \sim 100^\circ C$, the total pressure about 10 cmHg and the partial pressure ratio $NH_3 : CO_2 = 2 : 1$ is shown by the pressure—temperature (P—T) diagram in Fig. 3. The gas mixture does not react on curve A, but reacts on curve B, and the pressure change of curve B is larger with decreasing temperature. The dissociation of the product is plotted on curve C. The crosses on curve A shown the P- T relation of an innert gas, air.

(c) **The influence of the partial pressure.** The apparent yield derived from the pressure change at $-18^\circ C$ of the gas mixtures of three kinds of the partial pressure ratios is shown in Table 1. The excess of ammonia gives the higher yield than in the case of the partial pressure ratio $NH_3 : CO_2 = 2 : 1$, though the excess of carbon dioxide indicates the same yield at the constant intervals of time.

(d) **The influence of the water vapour.** The starting points of the reaction in the case of the gases dried only by passing through the drying materials are shown on curve

Table 1

Partial pressure ratio NH_3 : CO_2	Yield %
2.05 : 1.00	55
10.15 : 1.00	90
1.00 : 7.72	55

2 in Fig. 2. The position of curve 2 is lower by several centimeters at the same temperature than in the case of the gases dried by passing through the drying materials and preserving on phosphorus pentoxide, curve 1. Similarly in Fig. 3, in the case of the gases dried only by passing through the drying materials, curve 2, the pressure change is observed even at higher temperature by $20 \sim 30°C$ than in the case of the gases dried by passing through and preserving on the drying materials, curve 1.

(2) The reaction at high temperature and pressure.

(a) The isotherms. The PV—P curves, under the conditions of the temperature $50 \sim 200°C$, the total pressure $1 \sim 100$ atm and the partial pressure ratio $NH_3 : CO_2 = 2 : 1$, are shown in Fig. 4. Every isotherm has an inflexion point which indicates the reaction starts and the position of the point appears at high pressure with increasing temperature. At 129°C the curve is nearly monotonous. Below 129°C the white solid phase begins to appear at the conditions of the temperature and pressure of the inflexion point and disappear when the pressure is decreased at the same temperature. Above 129°C the whole space of the reaction vessel is occupied only with the gas phase and the reaction does not proceed so accurately reversible at the constant intervals of time as in the case below 129°C.
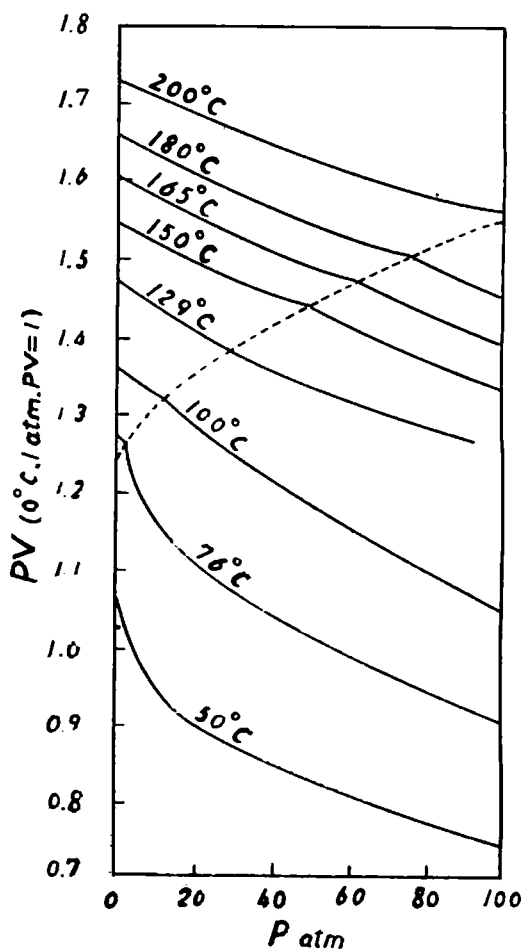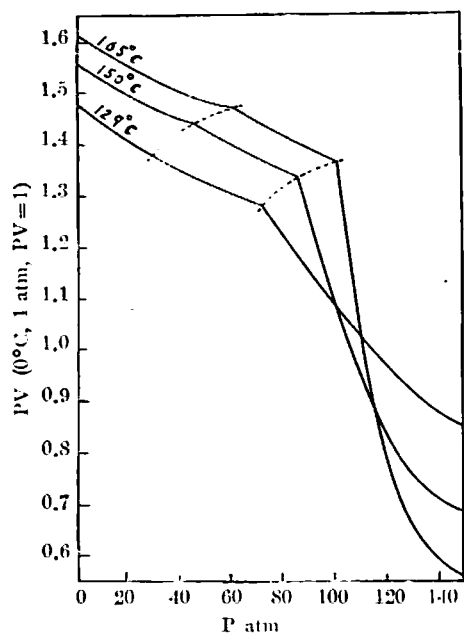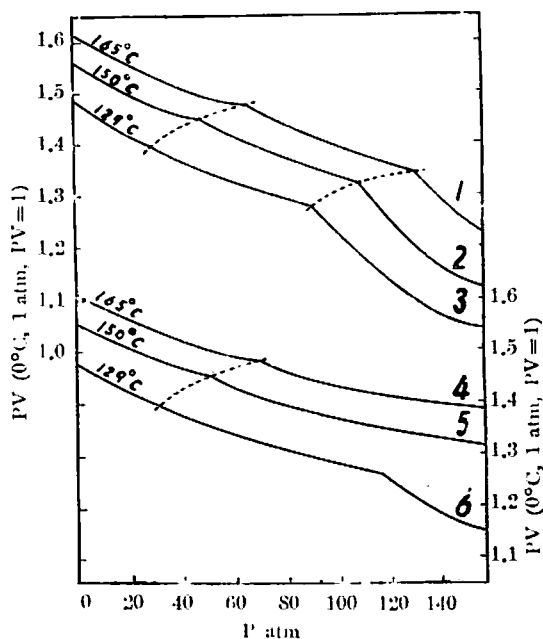
The PV—P curves, under the conditions of the temperatures 129, 150 and 165°C, the total pressure 1

Fig. 4 $NH_3 : CO_2 = 2 : 1$.

~ 100 atm and the partial pressure ratios $NH_3 : CO_2 = 3 : 1$, $2 : 1$ and $1 : 1$, are shown in Figs. 5, 6 and 7. Every isotherm has two inflexion points except in Fig. 7, in which the second inflexion point is found only at 129°C and not found

Fig. 5 $NH_3 : CO_2 = 3 : 1$.

Fig. 6   Curves 1, 2 and 3; $NH_3 : CO_2 = 2 : 1$.
Fig. 7   Curves 4, 5 and 6; $NH_3 : CO_2 = 1 : 1$.
The ordinates of Figs. 6 and 7 are shown by the right and left respectively.

at 150 and 165°C until 300 atm and the points shift to the side of high pressure with increasing temperature.

The whole space of the vessel is occupied only with the gas phase till the second inflexion point and after that produces a fog. The fog becomes droplets and the droplets enlarge with increasing pressure and finally the column of liquid appears on the head of mercury.

From the isotherms of Figs. 5, 6 and 7, in the case of excess ammonia, the first inflexion point is found to appear at somewhat lower pressure and the second point at considerably lower pressure, and the production velocity of the liquid phase is larger.

(b) The influence of the pressure. The relation between the reaction time and the apparent yield derived from the volume change under the conditions of the temperature 150°C, the total pressure 90 ~ 200 atm and the partial pressure ratios $NH_3 : CO_2 = 2 : 1$ and $3 : 1$, is shown in Fig. 8. The apparent yield becomes larger such as about 8, 12 and 16% respectively in 60 minutes and the time taken to reach equilibrium becomes shorter with increasing pressure from 110 to 150 and 200 atm in the case of the partial pressure ratio $NH_3 : CO_2 = 2 : 1$. On the other hand, the apparent yield becomes about 55% in 60 minutes at 90 atm

in the case of the partial pressure ratio $NH_3 : CO_2 = 3 : 1$ and reaches equilibrium within about 5 minutes at 150 atm and indicates the higher value than at 90 atm and the velocity of the volume change is too fast to draw the quantitative change of the diagram of the yield.

(c) **The influence of the water vapour.** The PV–P curves, when the gas mixture contains slightly the water vapour as mentioned in Exp. (1), (d), under the conditions of the temperature 165°C, the total pressure 1~160 atm and the partial pressure ratios $NH_3 : CO_2 = 3 : 1$, $2 : 1$ and $1 : 1$, show the same first and second inflexion
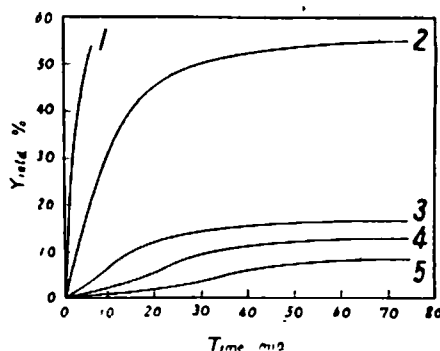

Fig. 8.
Curve 1; $NH_3 : CO_2 = 3:1$, 150°C, 150 atm.
Curve 2; $NH_3 : CO_2 = 3:1$, 150°C, 90 atm.
Curve 3; $NH_3 : CO_2 = 2:1$, 150°C, 200 atm.
Curve 4; $NH_3 : CO_2 = 2:1$, 150°C, 150 atm.
Curve 5; $NH_3 : CO_2 = 2:1$, 150°C, 110 atm.

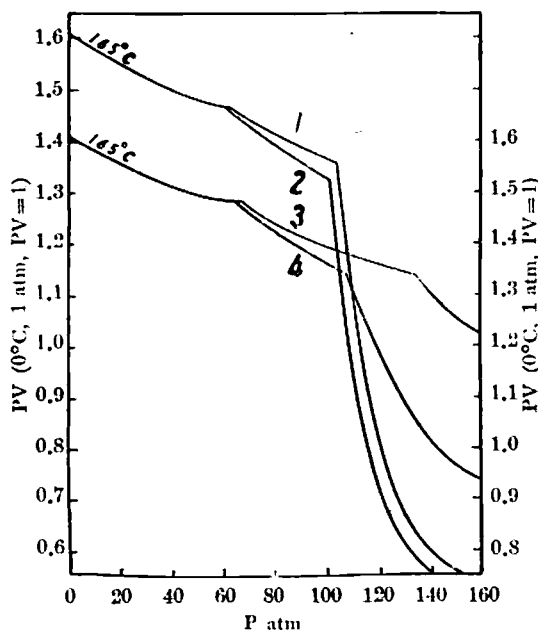

Fig. 9   Curves 1 and 2; $NH_3 : CO_2 = 3:1$, 165°C.
Fig. 10   Curves 3 and 4; $NH_3 : CO_2 = 2:1$, 165°C.
Curves 1 and 3 are the cases of the mixtures dried by passing through and preserving on the drying materials. Curves 2 and 4 are the cases of the mixtures dried only by passing through the drying materials. The ordinates of Figs. 9 and 10 are shown by the left and right respectively.
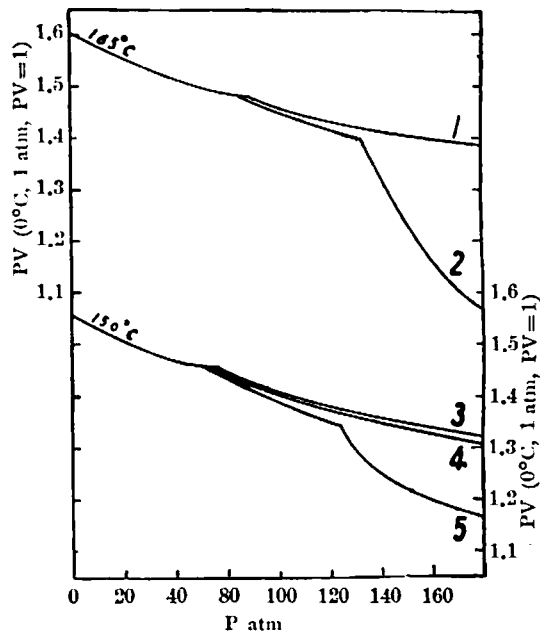
Fig. 11   Curves 1 and 2; $NH_3 : CO_2 = 1:1$, 165°C.
Fig. 12   Curves 3, 4 and 5; $NH_3 : CO_2 = 1:1$, 150°C.
Curves 1 and 3 are the cases of the mixtures dried by passing through and preserving on the drying materials. Curve 2 is the case of the mixture dried only by passing through the drying materials. Curves 4 and 5 are the cases of the mixtures added the water vapour 0.8 and 3% respectively. The ordinates of Figs. 11 and 12 are shown by the left and right respectively.

points at about 60 and 110 atm. The comparison between the PV–P curves of the gas mixture dried perfectly and the above mentioned curves is shown by Figs. 9, 10 and 11. In the curves of the gas mixtures are not found the difference between perfect and imperfect dryness till the first inflexion point appears, b t the gas dried imperfectly indicates the first inflexion point at somewhat lower pressure and the second inflexion point at considerably lower pressure, and after the points larger volume change occurs than the gas dried perfectly except in the case of the partial pressure ratio $NH_3 : CO_2 = 3 : 1$, Fig. 9.

The PV–P relation, in the cases of the addition of 0.8 and 3% water vapour to the gas mixture of the partial pressure ratio $NH_3 : CO_2 = 1 : 1$ at 150°C, is shown in Fig. 12. The liquid phase is not found at 250 atm in the cases of the dry gas mixture and the addition of 0.8% water vapour, but found at 110 atm in the case of 3% water vapour.

Consideration.

When the monotonous curve is inflected in the PV–P diagram of the gas mixture, the mixture begins either to react, or to condense under the condition of the inflexion point in the course of the compression. As shown in Fig. 4, it is considered that the white solid phase produced from the gas mixture under the condition of the inflexion point below 129°C is ammonium carbamate. The yield of ammonium carbamate becomes small with increasing temperature and in the case of 129°C the solid phase is scarcely found even after the inflexion point appears and the PV–P curve is almost monotonous. At the condition of the inflexion point above 129°C it is considered that the gas mixture produces urea and water in the gas state until it reaches saturation.

The comparison between the pressures, at which the mixtures produce the liquid phase as shown in Figs. 5 and 6, and the calculated vapour pressures of ammonium carbamate[3] at the same temperature is shown in Table 2. The pressures of the second inflexion point are independent of the calculated vapour pressures of ammonium carbamate. Accordingly, it can be considered that the gas mixture does not start to produce only the liquid phase of ammonium car-

Table 2

Condition $NH_3 : CO_2$ Temperature °C	Pressure atm		
	According to authors		Accord. to Egan
	3:1	2:1	2:1
129	73	93	29
150	86	110	61
165	102	133	104

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

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bamate at the second inflexion point, but the urea and water in the gas state produced from the gas mixture after the first inflexion point above $129°C$, reach saturation and start to condense.

Conclusion.

Below the normal temperature and pressure, the PV–P diagram of the gas mixture of ammonia and carbon dioxide indicates an inflexion point and the position shifts to the side of high pressure with increasing temperature and after the point the mixture produces ammonium carbamate. The lower the tempera- ture and the more excessive ammonia is, the larger the yield is at the constant intervals of time. The reaction is remarkably influenced by the water vapour slightly contained.

At high temperature and pressure, the PV–P curve of the gas mixture shows an inflexion point below $129°C$ and two inflexion points above $129°C$ and the position shifts to the side of high pressure with increasing temperature. Below $129°C$ the gas mixture produces ammonium carbamate and above $129°C$ starts the urea formation in the gas state at the first inflexion point. This indicates that the gas phase exist till the second inflexion point and begins to condense at the second point. The position of the condensation in the PV–P diagram is remarkably influenced by the total pressure, partial pressure ratio and water vapour.

The Laboratory of Physical Chemistry,
Kyoto University.