Equilibrium of the CO_2-NH_3-Urea-H_2O System under High Temperature and Pressure. I. Equilibrium Pressure of Reaction in Urea-Synthesis from Ammonia and Carbon Dioxide

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Introduction

In general, it is said that a content in a reaction vessel for the synthesis of urea from ammonia and carbon dioxide under high temperature and pressure is separated into two phases of melted solution and vapor.(1) But no one, so far as I know, has succeeded in analyzing plainly the equilibrium between the two phases in spite of the importance of industrial production of urea.

The writer has studied the equilibrium between the two phases of the CO_2-NH_3-Urea-H_2O system under high temperature and pressure.

The relations between the temperature and the equilibrium pressure of the reaction have been studied by several investigators.(1~4) The reported values as shown in Fig. 1 are divergent, while the experimental values(5) of the decomposition pressure of ammonium carbamate in the temperature range 10° to 80° are relatively fixed.

This paper covers a study of the equilibrium pressure of the reaction, in which loading mol ratio of carbon dioxide to ammonia is one by two, at the temperature range 130° to 170°, that is to say, in the absence of an excess of either reactant.

The experimental results showed that the equilibrium pressure 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. From this experimental facts the writer discusses the relations among the temperature, the equilibrium pressure and the loading density.

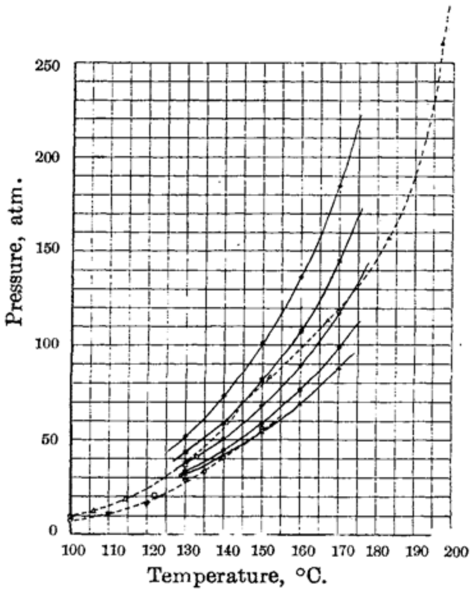

Fig. 1.—Pressure-temp. curves of the CO_2-NH_3-Urea-H_2O system. Loading density g./cc. of the present measurement: ◆, 1.0; ■, 0.8; ▼, 0.6; ●, 0.4; ▲, 0.2. Results given by other investigators: △, Briner (2); □, Fichter and Becker (3); ○, Matignon and Fréjacques (1); ▽, Tokuoka (4).

Experiment

The apparatus used for pressure measurements is shown in Fig. 2. The reaction vessel is made of steel with lead-lining and capacity is approximately 800 cc. For measuring pressure, the mercury trap of 20 cc. volnme was fixed between the reaction vessel and the Bourdon pressure gauge to prevent condensation of ammonium carbamate in it. The reaction vessel and the mercury trap were both dipped in a thermoregulated oil bath and heated at a given temperature for 20 to 24 hours. The container was loaded with crystalline ammonium carbamate or equi-molal mixture of urea and water.

Ammonium carbamate was prepared from refined gaseous carbon dioxide and ammonia in a glass vessel at ordinary temperature and pressure.

The same equilibrium pressure was obtained from the carbamate side of the reaction and also from the urea-water side on the same basis of initial loading density. Therefore, the equilibrium

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(1) Matignon and Fréjacques, *Compt. rend.*, **171**, 1003 (1920); *Bull. soc. chim.*, **31**, 394 (1922).

(2) Briner, *J. chim. phys.*, **4**, 266 (1906).

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

(4) Tokuoka, *J. Agr. Chem. Soc. Japan*, **11**, 174 (1935).

(5) Fgan, J. E. Potts and G. D. Potts, *Ind. Eng. Chem.*, **38**, 454 (1946).

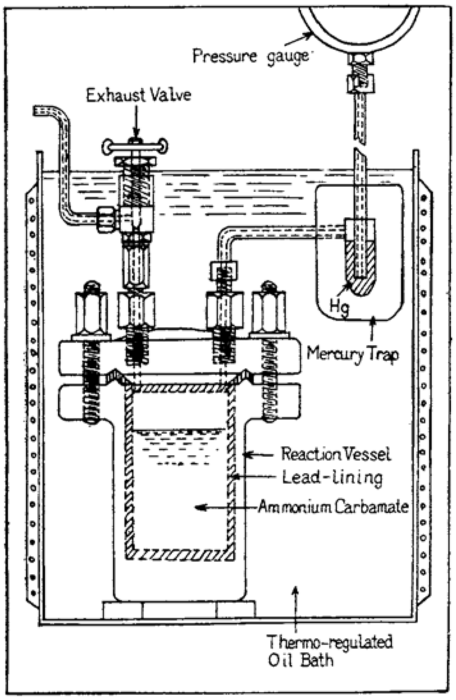

Fig. 2.—Apparatus for measuring the equilibrium pressure of the CO_2-NH_3-urea-H_2O system. I.

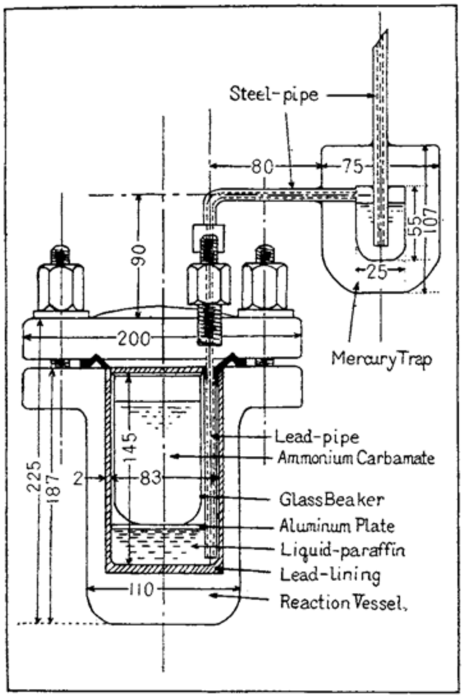

Fig. 3.—Apparatus for measuring the equilibrium Pressure of the CO_2-NH_3-Urea-H_2O system. II.

pressure is constant regardless of the kinds of starting materials at a given temperature and loading density.

In the preliminary experiments, the equilibrium pressure was measured after eliminating a small amount of residual air in the reaction vessel by a vacuum pump at ordinary temperature in the beginning of the experiment and then the last residual air together with carbamate decomposition gas at 100°. But in the other experiments in which these procedures were omitted, the same results were also obtained. Therefore, as the effect of residual air for the equilibrium pressure is very small, these procedures were omitted.

The writer measured the equilibrium pressure in the apparatus of Fig. 3 which is more corrosion-resistant than that of Fig. 2. The following device was made so that corrosive gas might not touch the mercury trap and the steel-pipe connecting between the former and the reaction vessel. Because both of the mercury trap and the steel trap have no lead-lining. The apparatus of Fig. 3 has a lead-pipe of inner diameter 3 mm. and length 14 cm., jointing to the cover of the reaction vessel and reaching almost to the bottom of the vessel where 60 cc. of liquid paraffin is charged. Ammonium carbamate is loaded in a glass beaker through an aluminum plate on the liquid paraffin. At a high temperature, carbamate decomposition gas compresses the liquid paraffin which arrives at the mercury-trap through the lead-pipe and steel-pipe. Therefore the gas in the apparatus touches only the glass and lead wall, aluminum plate and liquid paraffin, and no steel wall.

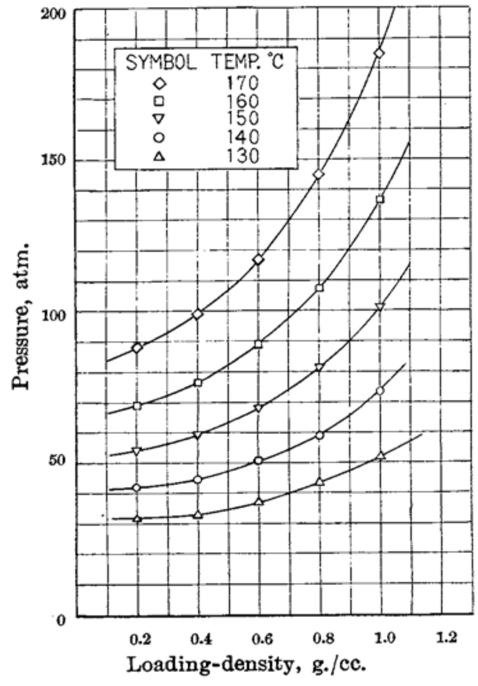

Fig. 4.—Equilibrium pressure-loading density curves of the CO_2-NH_3-Urea-H_2O system.

The experimental results of this apparatus were of the same values as those obtained in the experiments of the apparatus of Fig. 2. Therefore, the effect of corrosion of carbamate decomposition gas for the equilibrium pressure is negligible. The writer usually used the apparatus of Fig. 2.

Experimental Results

Experimental results on the relation of the loading density and the equilibrium pressure over the temperature range 130° to 170° are shown in Figs. 1 and 4. At a given temperature the equilibrium pressure increases with the loading density. Table 1 gives the experimental equations which show the relation between the temperature and the equilibrium pressure. Extrapolated values which were calculated at 180°, 200° and 250° from these equations are given in Table 2.

Table 1

Experimental Equations for Equilibrium Pressure-Temperature Relation of the CO_2-NH_3-Urea-H_2O System

Loading density, g./cc.	Experimental equation P=atm., T=absolute temp. °K.
0.20	$\log P=\frac{-1960}{T}+6.366$
0.40	$\log P=\frac{-2139}{T}+6.825$
0.60	$\log P=\frac{-2237}{T}+7.117$
0.80	$\log P=\frac{-2369}{T}+7.503$
1.00	$\log P=\frac{-2444}{T}+7.781$

Table 2

Extrapolated Values of Equilibrium Pressure at 180°, 200° and 250°C.

Loading density,	Equilibrium pressure, atm.		
g./cc.	180°C.	200°C.	250°C.
0.20	109	167	415
0.40	127	201	543
0.60	151	244	692
0.80	188	313	940
1.00	243	411	1280

Discussion of Results

Matignon and Frējacques(1) concluded already in 1920 that the system was bivariant, observing that the system consists of a vapor phase and a single homogeneous liquid phase, and assuming the following five reactions in the system.

$$CO(NH_2)(ONH_4) \rightleftarrows CO(NH_2)_2+H_2O \quad (1)$$

$$CO(NH_2)(ONH_4) \rightleftarrows CO_2+2NH_3 \quad (2)$$

$$CO(NH_2)(ONH_4)+H_2O \rightleftarrows CO_3(NH_4)_2 \quad (3)$$

$$CO_3(NH_4)_2 \rightleftarrows CO_3H(NH_4)+NH_3 \quad (4)$$

$$CO_3H(NH_4) \rightleftarrows CO_2+H_2O+NH_3 \quad (5)$$

They conjectured that the equilibrium pressure was a function of ratio of volume of the reaction vessel to initial content of carbamate in it at a given temperature.

Nevertheless, they could not only show these facts in their own experiments, but also their explanation that the system is bivariant is a mistake because the equation (5) is deduced from the other equations (2), (3) and (4).

In general, diversity of equilibrium pressure is a character proper to "the thermal dissociation compounds" such as CO_2-NH_3-H_2O system.(6)

Supposing an equilibrium system of the thermal dissociation compound is charged in a sealed vessel with changeable volume by the movement of a piston, an isothermal increase of the volume induces the vaporisation of a part of the liquid phase. And if the volume decreases isothermally, a part of the vapor is condensed. In both cases, the total pressure of the system and the compositions of the liquid and gas phases undergo some change, although the total composition of the system remains as it is.

For example, pure water has a constant vapor pressure at a given temperature. If the water vapor decomposes into hydrogen and oxygen as the following equation at the temperature below the critical point,

$$2\,H_2O \rightleftarrows 2\,H_2+O_2$$

hydrogen and oxygen would respectively dissolve into the liquid water with different solubility. Therefore, mol ratio of oxygen to hydrogen in the gas phase is not one by two and it will depend upon a ratio of initial content of water to volume of the vessel. At the same time the vapor pressure is indefinite and it will depend upon weight-volume ratio at the temperature.

By the above-mentioned qualitative explanation we can understand the diversity of the equilibrium pressure. In this paper the experimental results under the condition that

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(6) "Gmelins Handbuch der Anorganischen Chemie," **23**, Ammonium, p. 327, Verlag Chemie, G.m.b. H., Berlin, 1936.

loading mol ratio of carbon dioxide to ammonia is one by two have been described. In the next papers the writer will intend to report on the equilibrium pressure under such condition as loading mol ratio is less than one by two, that is, loading ammonia is in excess to carbon dioxide and the compositions of the liquid and gas phases quantitatively measured at various conditions of the loading density and the equilbrium pressure.

Summary

(1) In the study of the equilibrium pressure of the CO_2-NH_3-Urea-H_2O system, it was experimentally found that the equilibrium pressure of the system is a function of loading density of reactants in the reaction vessel at a given temperature.

(2) The experimental equations that show the relation between temperature and equilibrium pressure were studied at various loading densities, under conditions that loading mol ratio of carbon dioxide to ammonia was one by two, and at the temperature range 130° to 170°.

(3) It was verified that the diversity of the equilibrium pressure of the system is reasonable.

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