Equilibrium of the CO_2-NH_3-Urea-H_2O System under High Temperature and Pressure. III. Effect of Water Added on Liquid-Vapor Equilibrium

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It was found by Fichter and Becker(1) experimentally in 1911 that the initial presence of water has a strongly depressing influence on the conversion of ammonium carbamate to urea. This fact was later substantiated by several investigators. To date no one, however, has satisfactorily shown the effect of water added to ammonium carbamate on the liquid-vapor equilibrium of the system. The present paper covers a study of the variation

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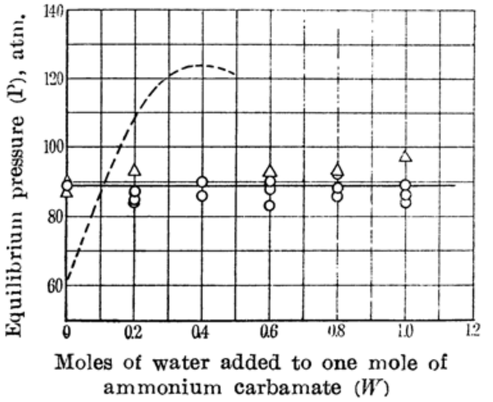
(1) Fichter and Becker, *Ber.*, **44**, 3473 (1911).

of the equilibrium pressure, the liquid and vapor compositions and densities with an increase in the amount of water in the original charge.

Measurements were begun after heating the system at 160°C. for 20 to 24 hours. Since the equilibrium of the system is dependent on the weight of the carbamate in a given reaction volume as reported in the previous paper,(2),(3), experiments were conducted in which the initial loading density of ammonium carbamate (D) was 0.60 g./cc. Mole ratio of water added to ammonium carbamate (W) was varied from 0.20 to 1.00. Consequently the total loading density including water added is over 0.60 g./cc.

Experimental Results and Discussion

Equilibrium Pressure: Results of investigation of the effect of water added on the equilibrium pressure which was measured from the carbamate side of the reaction and also from the urea and water side by means of an apparatus reported in the previous paper(2) are shown graphically in Fig. 1. The figure shows the equilibrium pressure to be approximately constant independent of mole ratio of water added to ammonium carbamate and of the kinds of starting materials within the experimental error. Only a study of the effect of water on the equilibrium pressure has been performed by N. W. Krase and V. L. Gaddy.(4) They showed that an increase in the percentage of water is accompanied by an increase in the total pressure of the charge as shown in Fig. 1, and gave a possible explanation that it is because of an increase in partial pressure of carbon dioxide as an increased percentage of ammonia was removed from the vapor phase on account of its greater solubility in water with increasing amount of water added. It is impossible to criticize their experiments since they made no reference to the apparatus and method of pressure measurement. Accordingly, the discrepancy between the two experimental results is obscure.

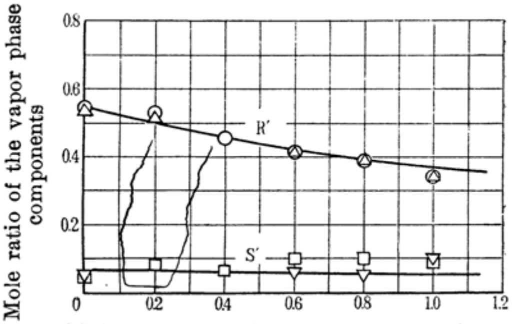


Moles of water added to one mole of ammonium carbamate (W)

Fig. 1.—Effect of water added to ammonium carbamate on the equilibrium pressure

Curve	Investigator	Temp. °C.	Initial Content
----	Krase and Gaddy(4)	150	Carbamate and Water
——	Present Measurement at $D=0.60$ g./cc.	160	○ Urea and Water △ Carbamate and Water

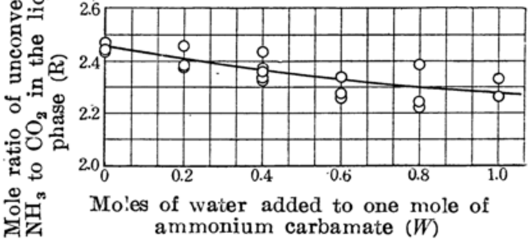
Vapor- and Liquid-Compositions: The effects of water added to the system on mole ratios (R' and S') of ammonia and water, respectively, to carbon dioxide in the vapor phase and on mole ratio (R) of unconverted ammonia to carbon dioxide in the liquid phase, measured by the methods reported in the previous paper,(3) are shown in Fig. 2 and 3 respectively. Both the



Moles of water added to one mole of ammonium carbamate (W)

Fig. 2.—Effect of water added to ammonium carbamate on the vapor composition at 160°C. and $D=0.60$ g./cc.

Symbol	Initial Content	Mole Ratio
○	Urea and Water	Ammonia to Carbon Dioxide (R')
△	Carbamate and Water	
□	Urea and Water	Water to Carbon Dioxide (S')
▽	Carbamate and Water	



Moles of water added to one mole of ammonium carbamate (W)

Fig. 3.—Effect of water added to ammonium carbamate on the liquid composition at 160°C. and $D=0.60$ g./cc.

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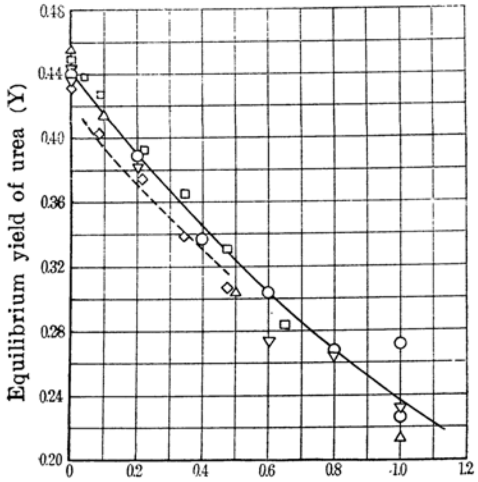
(2) S. Kawasumi, This Bulletin, **24,** 148 (1951).

(3) S. Kawasumi, ibid., **25,** 227 (1952).

(4) N. W. Krase and V. L. Gaddy, *J. Ind. Eng. Chem.*, **14,** 611 (1922).

vapor- and the liquid-compositions become richer in carbon dioxide with the increase of mole ratio (*W*) of water added to ammonium carbamate, and mole ratio (*S'*) of water to carbon dioxide in the vapor phase is approximately constant independent of the amount of water added.

Equilibrium Yield of Urea: It is evident that added water causes the equilibrium yield of urea to fall off, so that the best yield is obtained with pure ammonium carbamate. The results of the present study of the relation between the equilibrium yield of urea (*Y*) and mole ratio (*W*) of water added to ammonium carbamate are shown in Fig. 4 together with the results of other investigators.(4),(5),(6).

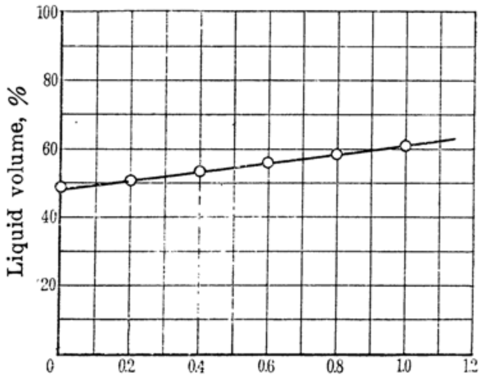


Moles of water added to one mole of ammonium carbamate (*W*)

Fig. 4.—Effect of water added to ammonium carbamate on the equilibrium yield of urea

Symbol	Investigator	Initial content	Temp., °C.	*D*, g./cc.
—○—	Present measurement	Urea and water	160	0.60
—▽—		Carbamate and water		
△	Kitawaki, Hori and Shimoda(6)		160	0.65
◇	M. Tokuoka(5)		150	0.50
□				0.90
------	Krase and Gaddy(4)		150	—

Volume of Liquid Phase: The relation between percentage of volume of the liquid phase, which was measured by the method reported in the previous paper,(3) and mole ratio (*W*) of water added to ammonium carbamate is shown in Fig. 5. The liquid volume increases linearly from 48.0% to 61.0% by the addition of one mole of water to one mole of ammonium carbamate.

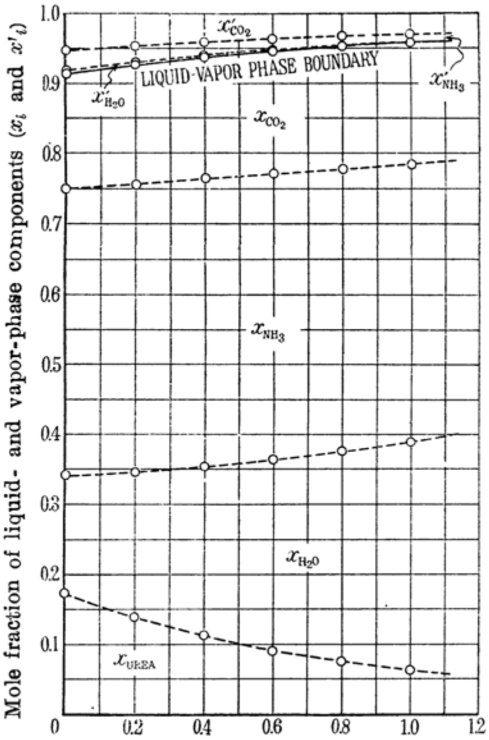


Moles of water added to one mole of ammonium carbamate (*W*)

Fig. 5.—Relation between liquid volume and water added at 160°C. and *D*=0.60 g./cc.

Effect of Water on Liquid-Vapor Equilibrium Compositions

The liquid-vapor equilibrium compositions at 160°C. and *D*=0.60 g./cc., which were calculated from the above-mentioned data on the same assumption and by the same method



Moles of water added to one mole of ammonium carbamate (*W*)

Fig. 6.—Liquid-vapor equilibria diagram of the CO_2-NH_3-Urea-H_2O system in the presence of water added.
(Temp.=160°C. and *D*=0.60 g./cc.)

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

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

Table 1

Effect of Water Added to Ammonium Carbamate on Liquid and Vapor Phase Compositions in Equilibrium State at 160°C. and $D=0.60$ g./cc.
($c=7.685$ mole/l.)

W, mole water/mole carbamate			0	0.20	0.40	0.60	0.80	1.00
P, atm.			89	89	89	89	89	89
R'			0.547	0.500	0.460	0.425	0.395	0.370
S'			0.066	0.062	0.060	0.057	0.056	0.054
R			2.460	2.410	2.365	2.330	2.300	2.275
Y			0.442	0.390	0.345	0.304	0.268	0.237
Equilibrium Concentration,	mole/l.	n'_{CO_2}	1.031	1.006	0.964	0.927	0.886	0.847
		n'_{NH_3}	0.564	0.503	0.444	0.394	0.350	0.313
		n'_{H_2O}	0.068	0.062	0.058	0.053	0.050	0.046
		n_{CO_2}	3.257	3.682	4.070	4.422	4.740	5.016
		n_{NH_3}	8.012	8.873	9.624	10.304	10.902	11.413
		n_{Urea}	3.397	2.997	2.651	2.336	2.059	1.822
		n_{H_2O}	3.329	4.472	5.667	6.894	8.157	9.461
	mole fraction	N'_{CO_2}	0.620	0.640	0.658	0.674	0.690	0.702
		N'_{NH_3}	0.339	0.320	0.303	0.287	0.272	0.260
		N'_{H_2O}	0.041	0.040	0.039	0.039	0.038	0.038
		N_{CO_2}	0.181	0.184	0.185	0.185	0.183	0.181
		N_{NH_3}	0.445	0.443	0.437	0.430	0.422	0.412
		N_{Urea}	0.189	0.150	0.120	0.097	0.080	0.066
		N_{H_2O}	0.185	0.223	0.258	0.288	0.315	0.341
d', g./cc.			0.109	0.109	0.108	0.110	0.110	0.111
d, g./cc.			1.131	1.133	1.139	1.132	1.135	1.139
K_{N_1}			0.974	0.926	0.876	0.817	0.773	0.733

as reported in the previous paper,(3) are shown in Table 1. A plot of mole fraction (x_i and x'_i) of components in the two phases against mole ratio (W) of water added to ammonium carbamate is drawn in Fig. 6. From these results, it has become evident that a large percentage of water added to the system exists in the liquid phase, and consequently the volume of the liquid phase increases with an increase of the amount of water added. It may be concluded that the constancy of the equilibrium pressure independent of the amount of water added to the system is because of a decrease in total mole of components in the vapor phase on account of their greater solubility in water as well as of a decrease in the volume of the vapor phase with an increase of the amount of water added.

The equilibrium constants K_{N_1} of the following reaction represented by mole fraction N_i

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

$$K_{N_1}=\frac{N_{Urea}N_{H_2O}}{N_{CO_2}N^2_{NH_3}}$$

are shown in the last line of Table 1. As the values of K_{N_1} show a tendency to decrease gradually with an increase of water added to the system at a given temperature, K_{N_1} is not an equilibrium constant in the true sense of the term. The equilibrium constant should be calculated on the other assumption and discussed from the other stand-point.

Liquid- and Vapor-Density

Results of calculation of the liquid- and vapor-density (d and d') at 160°C. and over the range of mole ratio (W) from 0.20 to 1.00 of water added to ammonium carbamate are shown in Table 1. Both densities are approximately constant independent of the amount of water added. In general, the vapor-density increases linearly with the rise of pressure as shown in the previous paper.(3) Therefore, the constancy of the equilibrium pressure independent of the amount of water added will also be reasonable from the results of calculation of the vapor-density, since it undergoes little change by the addition of water.

Summary

(1) The effect of water added to ammonium

carbamate on liquid-vapor equilibrium of the CO_2-NH_3-Urea-H_2O system was investigated at 160°C. and a loading density of ammonium carbamate 0.60 g./cc. and over the range of mole ratio from 0.20 to 1.00 of water added to ammonium carbamate.

(2) The equilibrium pressure is approximately constant independent of the amount of water added within the range of the experimental conditions. Both the vapor- and the liquid-compositions become richer in carbon dioxide, and the equilibrium yield of urea decreases with an increase of the amount of water added.

(3) The results of calculation of the compositions and densities of the liquid- and the vapor-phases in the equilibrium state when water ranging from 0.20 to 1.00 mole was added to one mole of ammonium carbamate have been shown.

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