Equilibrium of the CO_2—NH_3—Urea—H_2O *System under High Temperature and Pressure. V. Liquid-Vapor Equilibrium in the Presence of Excess Ammonia or Carbon Dioxide*[1]

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The liquid-vapor equilibrium compositions in a reaction vessel for urea synthesis from ammonia and carbon dioxide under high temperature and pressure have previously been shown in the stoichiometrical loading mole ratio of $2NH_3$ to 1 CO_2[2], assuming 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.

For the purpose of presenting similarly the compositions of the liquid and vapor phases of the equilibrium system starting with a mixture of ammonium carbamate and excess amount of ammonia or carbon dioxide in this paper, the yield of urea and the mole ratios of unconverted ammonia to carbon dioxide in the liquid phase of the system have been measured at a temperature of 160°C. The compositions of the system have been calculated from the present and the previous measurements[3] over the range of the loading NH_3-CO_2 mole ratio (L) from 1.6 to 3.0.

On the basis of these results, the effects of the variation of the loading mole ratio on the equilibrium compositions and the equilibrium constant of the following reaction have been discussed.

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

Relation between Loading Composition and Equilibrium Yield of Urea. It is an established fact that the excess ammonia over the stoichiometrical 2 moles per mole of carbon dioxide causes an increase of the equilibrium yield of Urea (Y_c) based on the quantity of the initially charged carbon dioxide. The present measurements of the urea yield under conditions where the excess ammonia or carbon dioxide was added to the carbamate, which was loaded with a constant density of 0.60 g./cc., are plotted against the reciprocal of L in Fig. 1.

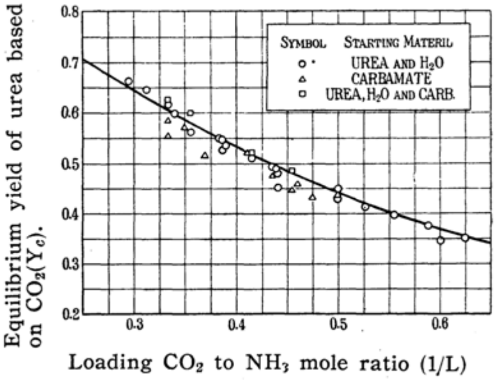

Fig. 1.—Y_c—1/L relation at 160°C. and $D=0.60$ g./cc.

Y_c was measured by the following procedure: after the system reached the equilibrium, the reaction vessel was rapidly cooled and then the content was withdrawn. Water and unconverted NH_3 and CO_2 were completely evaporated out of the content at 70°C. and the amount of residual urea was weighed.

The urea yield (Y_a) based on the quantity

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[1] This paper was presented at the annual meeting of the Chemical Society of Japan held at Kyoto University, on April 2, 1953.

[2] S. Kawasumi, This Bulletin, **25**, 227 (1952).

[3] S. Kawasumi, ibid., **26**, 222 (1953).

of the initially charged ammonia, which is connected with Y_c by the equation: $Y_a \times L = 2Y_c$ is approximately constant independent of L over the range of $L<2$, while it decreases with the rise of L over the range of $L>2$.

It is a remarkable fact that the Y_c-L relation at a constant temperature and loading density depends upon the definition of the loading density. In the present experiments as mentioned above, the starting materials were prepared by loading ammonium carbamate or equi-molar urea and water into the reaction vessel with a constant loading density (D), followed by the addition of the required amount of ammonia or carbon dioxide to it. Consequently, the total loading density (D_t) including excess ammonia or carbon dioxide was varied over the range of L. Regarding the molecular weights of NH_2COONH_4, NH_3 and CO_2 as 78, 17 and 44 respectively, $D_t = \frac{D}{78}(44+17L)$ over the range of $L>2$ and $D_t = \frac{2D}{78L}(44+17L)$ over the range of $L<2$. In this case, therefore, D_t is the minimum at $L=2$ as shown in Fig. 2.

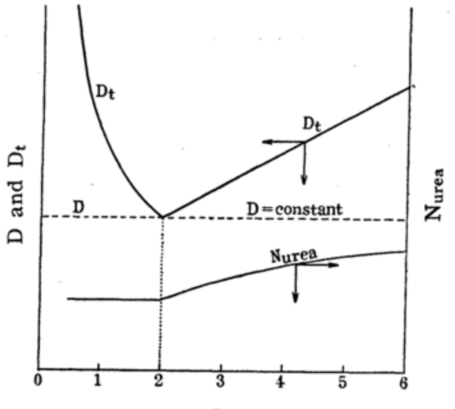

Fig. 2.—D_t—L relation in the experiment performed with a constant D.

If an experiment would be performed with a constant D_t, it would be conjectured that the amount of urea (n_{urea}) in the unit volume of the reaction vessel attains to the maximum at a certain loading mole ratio, since the loading density (D) of the carbamate is the maximum at $L=2$ as shown schematically in Fig. 3. Therefore it may be concluded that the Y_c-L relation at a constant D_t is undoubtedly different from that at a constant D.

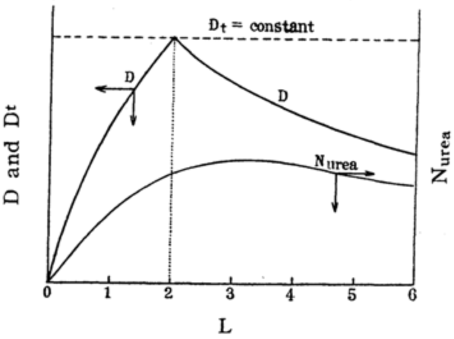

Fig. 3—D—L relation in the experiment performed with a constant D_t.

The existence of an optimum temperature where Y_c attains to the maximum has already been discussed in the previous paper2) under conditions where ammonia and carbon dioxide were used in the stoichiometrical proportion to form ammonium carbamate and the loading density of the carbamate was kept constant. Similarly in the presence of excess ammonia or carbon dioxide, the optimum temperature where Y_c attains to the maximum rises with an increase of D at a given L and also it rises with an increase of L at a given D. Such the Y_c-L-T-D relations may be explained to be based upon the same reason as described in the previous paper2).

Relation between Loading-and Liquid-Composition—Under conditions where carbamate was charged at a loading density of 0.60 g. per cc. of a reaction vessel and then 0.2 to 1.0 moles of excess ammonia or 0.05 to 0.25 moles of carbon dioxide was added to one mole of the carbamate, the mole ratio (R) of unconverted ammonia to carbon dioxide in the liquid phase has been measured at 160°C. by the method reported in the previous paper.2)

The experimental results are shown in Fig. 4. It has previously been shown that R' increases with L under the same conditions2). R also increases with L.

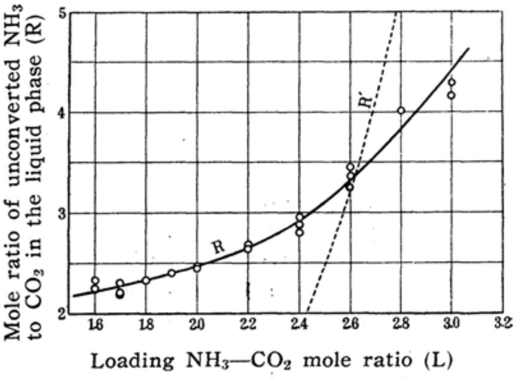

Fig. 4.—R—L relation at 160°C. and D=0.60 g./cc.

Relation between Equilibrium Composition and Loading NH_3-CO_2 Mole Ratio—A method for calculating the equilibrium concentration of each component in the two phases on the same assumption as previously employed[2] is shown in such a case as that where "c" moles of ammonium carbamate (equivalent of "$2c$" moles of ammonia and "c" moles of carbon dioxide) were initially loaded into a reaction vessel of one litre volume and then "m" moles of excess ammonia or carbon dioxide were added to one mole of the carbamate.

Equations giving Concentrations in the Presence of Excess Ammonia—In this case ($L=2+m$), we obtain from the material balance respectively,

$$n_{\text{urea}}+n_{CO_2}+n'_{CO_2}=c \quad \cdots\cdots\cdots\cdots(2)$$

$$2n_{\text{urea}}+n_{NH_3}+n'_{NH_3}=(2+m)c \cdots\cdots\cdots(3)$$

Let us put,

$$n'_{NH_3}\ /\ n'_{CO_2}=R' \quad \cdots\cdots\cdots\cdots\cdots(4)$$

$$n'_{H_2O}\ /\ n'_{CO_2}=S' \cdots\cdots\cdots\cdots\cdots\cdots(5)$$

$$n_{NH_3}\ /\ n_{CO_2}=R \quad \cdots\cdots\cdots\cdots\cdots\cdots(6)$$

$$n_{\text{urea}}=cY_c \cdots\cdots\cdots\cdots\cdots\cdots\cdots(7)$$

and

$$n_{H_2O}=n_{\text{urea}}-n'_{H_2O} \quad \cdots\cdots\cdots\cdots\cdots(8)$$

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

$$n'_{CO_2}=\frac{c}{R-R'}\{(1-Y_c)(R-2)-m\} \quad \cdots(9)$$

$$n'_{NH_3}=\frac{cR'}{R-R'}\{(1-Y_c)(R-2)-m\}\cdots(10)$$

$$n'_{H_2O}=\frac{cS'}{R-R'}\{(1-Y_c)(R-2)-m\}\cdots(11)$$

$$n_{CO_2}=\frac{c}{R-R'}\{(1-Y_c)(2-R')-m\}\cdots(12)$$

$$n_{NH_3}=\frac{cR}{R-R'}\{(1-Y_c)(2-R')-m\}\cdots(13)$$

$$n_{\text{urea}}=cY_c \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots(7')$$

$$n_{H_2O}=c\left[Y_c-\frac{S'}{R-R'}\{(1-Y_c)(R-2)-m\}\right] \quad (14)$$

Equations giving Concentrations in the Presence of Excess Carbon Dioxide—Similarly in this case ($L=\frac{2}{1+m}$), we obtain the equations (15) and (16) from the material balance.

$$n_{\text{urea}}+n_{CO_2}+n'_{CO_2}=(1+m)c \cdots\cdots(15)$$

$$2n_{\text{urea}}+n_{NH_3}+n'_{NH_3}=2c \cdots\cdots\cdots(16)$$

In the same way from these two equations and the above five equations (4) to (8), we can derive the following relations, for example n'_{CO_2} and n_{CO_2}, which allow the equilibrium concentration to be calculated.

$$n'_{CO_2}=\frac{c}{R-R'}\{(1-Y_c)(R-2)+m\cdots\}(17)$$

$$n_{CO_2}=\frac{c}{R-R'}\{(1-Y_c)(2-R')-mR'\} \quad (18)$$

Equilibrium Compositions in the Presence of Excess Ammonia and Carbon Dioxide—The liquid and vapor phase compositions have been calculated from these equations, as shown in Table 1, under the conditions

TABLE I

LIQUID-VAPOR EQUILIBRIUM COMPOSITIONS IN THE PRESENCE OF EXCESS AMMONIA OR CARBON DIOXIDE AT 160°C. AND D=0.60 g/cc

	L	1.60	1.80	2.00	2.20	2.40	2.62	2.80	3.00
	c, mole/l.	7.685	7.685	7.685	7.685	7.685	7.685	7.685	7.685
	excess CO_2, mole/l.	1.921	0.854	—	—	—	—	—	—
	excess NH_3, mole/l.	—	—	—	1.537	3.074	4.764	6.149	7.685
	P, atm.	151	114	89	76	66	69.5	75	80
	R′	0.156	0.287	0.547	1.035	1.850	3.380	5.350	9.250
	S′	0.025	0.040	0.066	0.110	0.175	0.260	0.375	0.575
	R	2.220	2.330	2.460	2.618	0.925	3.380	3.827	4.390
	Yc	0.355	0.398	0.442	0.483	0.517	0.551	0.577	.0604
Concentration, mole/l.	n'_{CO_2}	2.520	1.664	1.031	0.579	0.346	0.203	0.136	0.084
	n'_{NH_3}	0.393	0.478	0.564	0.600	0.639	0.684	0.730	0.781
	n'_{H_2O}	0.063	0.067	0.068	0.064	0.061	0.053	0.051	0.049
	n_{CO_2}	3.676	3.474	3.257	3.395	3.364	3.247	3.114	2.959
	n_{NH_3}	8.150	8.100	8.012	8.887	9.854	10.980	11.915	12.990
	n_{urea}	3.410	3.400	3.397	3.710	3.975	4.235	4.435	4.640
	n_{H_2O}	3.347	3.334	3.329	3.646	3.915	4.182	4.384	4.591
Equilibrium mole fraction	N'_{CO_2}	0.874	0.754	0.620	0.466	0.330	0.216	0.149	0.092
	N'_{NH_3}	0.132	0.216	0.339	0.483	0.612	0.728	0.795	0.855
	N'_{H_2O}	0.021	0.030	0.041	0.051	0.058	0.056	0.056	0.053
	N_{CO_2}	0.198	0.190	0.181	0.173	0.160	0.143	0.130	0.118
	N_{NH_3}	0.439	0.442	0.445	0.453	0.467	0.485	0.500	0.516
	N_{urea}	0.184	0.186	0.189	0.189	0.188	0.187	0.186	0.184
	N_{H_2O}	0.180	0.182	0.185	0.185	0.185	0.185	0.184	0.182
	$K_{N\text{-}(1)}$	0.870	0.911	0.974	0.985	1.000	1.025	1.049	1.073

where the equilibrium was established at 160°C. starting with a mixture prepared by loading ammonium carbamate of $c=7.685$ moles at a constant density of $D=0.60$ g./cc. into a reaction vessel of one litre volume, followed by adding a required excess amount of ammonia or carbon dioxide to the carbamate. Accordingly the total loading densities including excess ammonia or carbon dioxide are more than 0.60 g./cc. at any loading NH_3-CO_2 mole ratio.

With the increase of the excess amount of carbon dioxide added to the carbamate, the equilibrium pressure³⁾ rises remarkably and also Y_a is approximately constant independent of the excess amount of carbon dioxide as explained above. According to the calculation, these experimental results are undoubtedly based upon the fact that carbon dioxide is increased not in the liquid, but in the vapor phase. The table also indicates that the larger amounts of the excess ammonia initially added to the carbamate mostly exist in the liquid phase, so that the liquid volume may possibly increase with the excess amount of ammonia.

The liquid-vapor equilibrium diagram of the system at 160°C. is represented as a plot of x_i against L in Fig. 5. As shown in this diagram, x_{urea} and x_{H_2O} attain respectively to the maximum, since an increase of the excess amount of ammonia in the original charge is accompanied by an increase of n_{urea} and n_{H_2O} as well as the total sum of moles (X) of every component in both liquid and vapor phases.

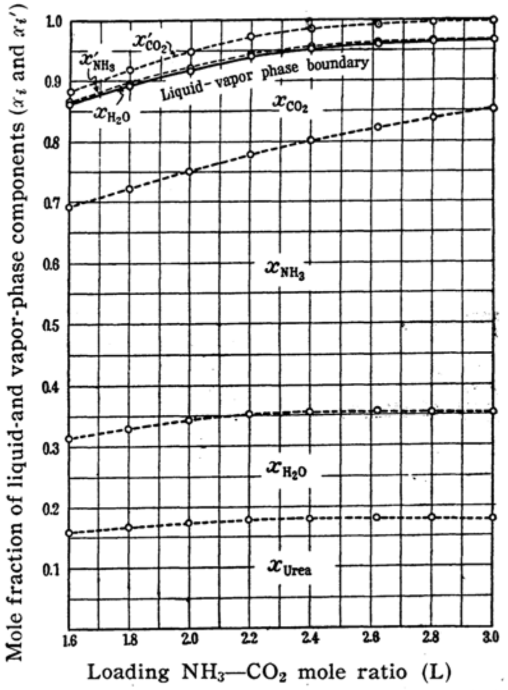

Fig. 5.—Liquid-vapor equilibria diagram of the CO_2—NH_3—Urea—H_2O system in the presence of excess ammonia or carbon dioxide at 160°C.

According to the results of Table 1, the amount of urea is approximately equal to that of water in the liquid phase due to the small amount of water vapor, so that a molecular compound of urea-water, $(NH_2)_2CO\cdot H_2O$, may be assumed for the purpose of expressing the liquid-vapor equilibrium compositions as the three component system, as such an expedient has already been employed by Davis and Black.⁴⁾

In such a manner, a ternary diagram with the apices representing the three constituents—ammonia, carbon dioxide, and water in the vapor or urea-water in the liquid—has also been illustrated from the above data as shown in Fig. 6.

Three pressure-composition diagrams for the systems consisting of every two constituents of them are also given in Fig. 6–A, –B and –C. At a temperature of 160°C. the system exerts the minimum pressures at a point "*a*" on a vapor curve where the vapor is composed of ammonia and carbon dioxide in the stoichiometrical proportion to form ammonium carbamate, or $R'=2$, and this point is in equilibrium with a point "*b*" on a liquidus curve which has the composition of $R=2.925$. The coexisting two points of "*c*" on the vapor curve and "*d*" on the liquidus curve have the same mole ratio of ammonia to carbon dioxide, that is, $R=R'=3.38$. Usually in the binary system an azeotropic mixture in which the coexisting liquid and vapor have the same composition exerts the maximum or minimum pressure at a constant temperature. It will be seen in this diagram that "*a*" and "*b*" are not necessarily consistent with "*c*" or "*d*" in the system of three or more components such as the present system.

Further consideration will be given to the point where the coexisting liquid and vapor have the same composition. At this point,

$$R=R' \quad \cdots\cdots\cdots\cdots(19)$$

By the definitions of L and Y_c and from the material balance,

$$L=\frac{n_{NH_3}+n'_{NH_3}+2n_{\text{urea}}}{n_{CO_2}+n'_{CO_2}+n_{\text{urea}}} \qquad (20)$$

$$Y_c=\frac{n_{\text{urea}}}{n_{CO_2}+n'_{CO_2}+n_{\text{urea}}} \qquad (21)$$

By eliminating all of n_{CO_2}, n'_{CO_2}, n_{NH_3}, n'_{NH_3} and n_{urea} from these five equations of

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4) Davis and Black, *Ind. Eng. Chem.*, **23**, 1280 (1931).

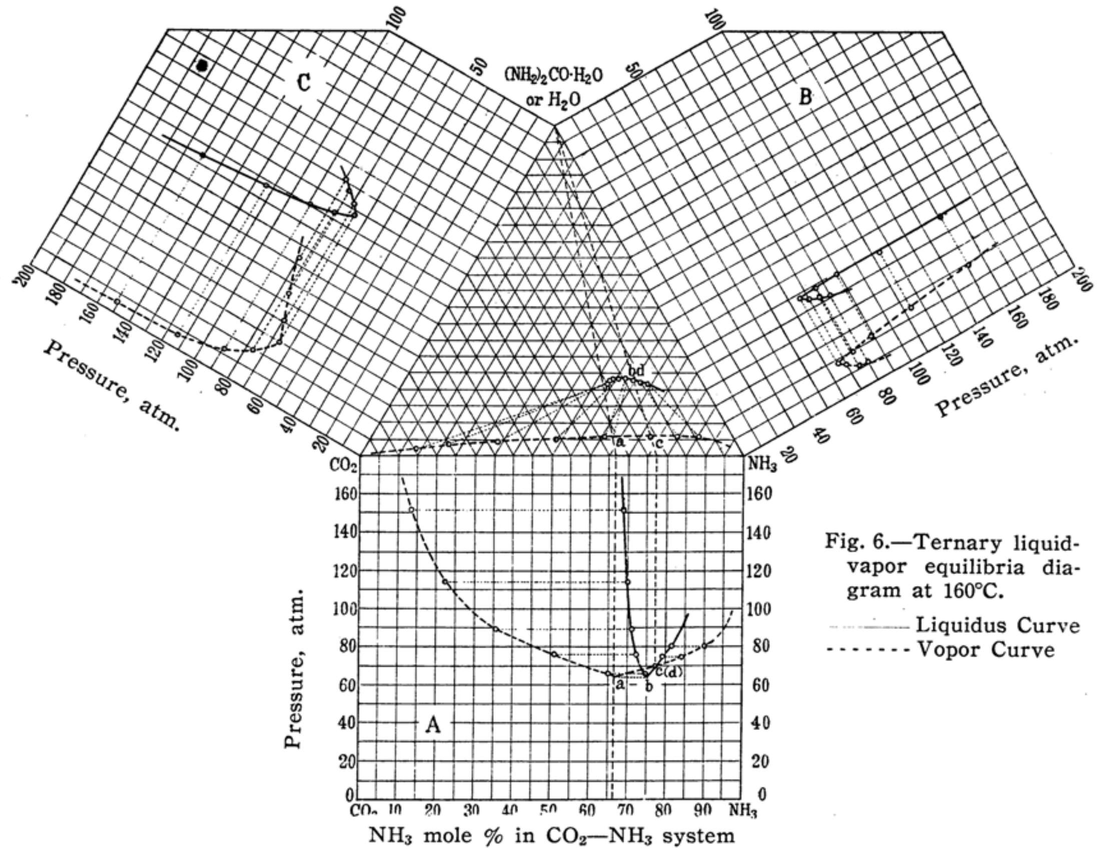

Fig. 6.—Ternary liquid-vapor equilibria diagram at 160°C.
—·—·— Liquidus Curve
- - - - - - - Vopor Curve

(4), (6), (19), (20) and (21), the following relation is derived:

$$L-2=(1-Y_c)\,(R-2)=(1-Y_c)\,(R'-2) \qquad (22)$$

The present experiments under the condition of $T=160$°C. and $D=0.60$ g./cc. showed the observed values of $R=R'=3.38$ and $Y_c=0.551$ at $L=2.62$ to be in accord with the relation represented by the equation (22).

The equilibrium constants ($K_{N-(1)}$) of the reaction (1) at 160°C. represented by mole fraction (N_i) of each component in the liquid phase ($K_{N-(1)}=\dfrac{N_{\text{urea}}\,N_{H_2O}}{N_{CO_2}\,N_{NH_3}{}^2}$) are also given in the last line of Table 1. As these values show a tendency to increase gradually with L at a constant temperature, $K_{N-(1)}$ is not an equilibrium constant in the true sense of the term as described in that case in which water has been added to mmonium carbamate.[5] The equilibrium constant should be calculated on the other assumption and explained from the other stand-point in further discussion.

Liquid Volume and Densities—Under the conditions of $T=160$°C. and $D=0.60$ and 0.40 g./cc., the liquid-vapor volume ratios in the presence of the excess amount of ammonia have been measured over the range of $L=2.0\sim3.0$ by a method which was described in the previous paper.[2] The percentage of the liquid volume to the vessel volume increases linearly with L as shown in Fig. 7. The liquid and vapor densities of the system under high temperature and pressure are given by dividing the weight of each phase obtained from Table 1 by the liquid-and vapor-volume respectively. The

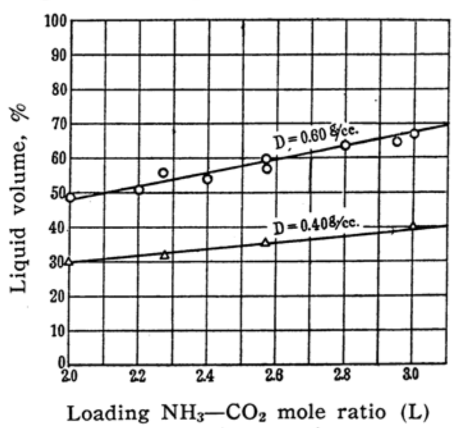

Fig. 7.—Liquid volume in the presence of excess ammonia at 160°C.

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[5] S. Kawasumi, This Bulletin, **26**, 218 (1953).

densities (d and d') of the two phases decrease with L, and d′ attains to the minimum at $L=2.7\sim2.8$ as shown in Fig. 8.

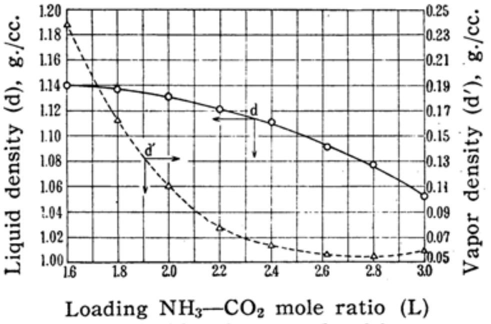

Fig. 8.—Liquid-and vapor-densities over the range of $L=1.6\sim3.0$ at $T=160°C$. and $D=0.60$ g./cc.

Summary

The liquid-vapor equilibrium compositions of the CO_2-NH_3-Urea-H_2O system starting with a mixture of ammonium carbamate and the excess amount of ammonia or carbon dioxide have been calculated at 160°C. and over the range of the loading NH_3-CO_2 mole ratio of 1.6 to 3.0 from the experimental data presented in the previous paper of this series.

The effects of the loading NH_3-CO_2 mole ratio on the equilibrium compositions have been discussed and the liquid-vapor equilibrium diagram of the system in the presence of excess ammonia or carbon dioxide has been drawn.

Symbols	**Nomenclature**
c	—Number of moles of ammonium carbamate loaded initially into the reaction vessel, gram mole per litre
d	—Density of liquid, gram per cc.
D	—Loading density, or ratio of the weights of materials to the total volume of the reaction vessel, gram per cc.
D_t	—Total loading density including excess ammonia or carbon dioxide, gram per cc.
$K_{N-(1)}$	—Equilibrium constant of the reaction$^{(1)}$ represented by mole fraction N_i, no units
L	—Loading ammonia-carbon dioxide mole ratio, no units
m	—Number of moles of excess ammonia or carbon dioxide to one mole of ammonium carbamate, 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
T	—Temperature, °C.
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
X	—Total sum of moles of every component of the two phases, per litre of the reaction vessel, gram mole per litre
Y_c	—Equilibrium yield of urea based on carbon dioxide in the original charge, or ratio of gram moles of urea to initial loading moles of carbon dioxide, no units
Y_a	—Equilibrium yield of urea based on ammonia in the original charge, no units

Superscript

′(dash) —sign to denote the vapor phase

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