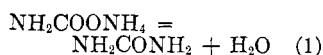


Equilibria in the Ammonium Carbamate-Urea-Water System

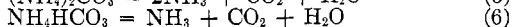
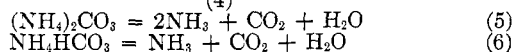
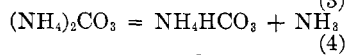
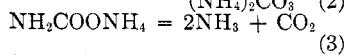
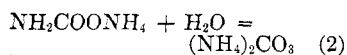
K. G. CLARK, V. L. GADDY, AND C. E. RIST

Fertilizer and Fixed Nitrogen Investigations, Bureau of Chemistry and Soils, Washington, D. C.

THE transformation of ammonium carbamate into urea produces equimolal quantities of urea and water as expressed by the equation:



Ammonium carbamate reacts with water to form ammonium carbonate, and upon vaporization dissociates into ammonia and carbon dioxide. These facts lead to the following series of side reactions increasing the complexity of the system:



Bassarov (1) discovered in 1870 that urea was produced when ammonium carbamate was heated in sealed glass tubes at 130° to 140° C. Bourgeois (2) demonstrated in 1897 that urea could be produced not only from ammonium carbonate but also from other carbon dioxide compounds of ammonia when he obtained yields of 1.5 to 9.52 per cent urea by heating the carbamate, the carbonate, the sesquicarbonate, and the bicarbonate to 130° C. in a steel reactor. He noted that the steel was rather strongly attacked under the conditions of his experiments. According to the data of Briner (3) and of Isambert (7) ammonium carbamate exerts a dissociation pressure of approximately 1, 38, and 260 atmospheres at 60°, 130°, and 197° C., respectively.

Since Bassarov and Bourgeois numerous investigators have studied the equilibria in this system, reporting their results in terms of the percentage conversion of the carbamate expressed as percentage yield of urea. Fichter and Becker (5) in 1911 and Fichter, Steiger, and Stanisch (6) in 1917 studied the formation of urea from ammonium carbamate in a tin-lined reactor over the temperature range 100° to 140° C. Fichter and Becker reported increased yields of urea with an increase in the weight-volume ratio of the system and an optimum conversion temperature of approximately 135° C. Fichter, Steiger, and Stanisch obtained increased yields of urea with moderate excesses of ammonia. Lewis and Burrows (11) in 1912 determined the equilibrium in aqueous solutions between 77° and 132° C. Matignon and Frejacques (13) in 1920, observing the system to consist of a vapor phase with a single homogeneous liquid phase, concluded that the system was bivariant. They further pointed out that increasing yields of urea were to be expected with decreasing vapor-phase volumes or increasing weight-volume ratios as Fichter and Becker had determined experimentally. The work of Matignon and Frejacques carried out in sealed

The degree of conversion of ammonium carbamate into urea and water is determined from both sides of the reaction over the temperature range 135° to 200° C. in Rezistal No. 4 reactors at a weight-volume ratio of 0.9 gram per cc. Similar data are obtained starting from the urea-water side of the reaction in sealed glass tubes at the higher weight-volume ratio of 1.0 gram per cc. The yields of urea are in every case higher than those obtained by other investigators working at lower weight-volume ratios.

The effect of the variation of the weight-volume ratio on the yield of urea is studied in sealed glass tubes at 170° C. The range covered is 0.2 to 1.0 gram per cc. Empirically the yield of urea is found to be a linear function of the reciprocal of the weight-volume ratio.

glass tubes at temperatures from 130° to 150° C. with a weight-volume ratio of approximately 0.5 gram per cc., a value somewhat higher than had previously been used, showed correspondingly higher yields of urea. Various investigators at this laboratory have studied this system with regard to its industrial application for the synthesis of urea from ammonia and carbon dioxide. Many experiments have been carried out in tin-lined and in Rezistal No. 4 reactors, as well as in glass tubes, up to temperatures of 150° C. The results of much of this work have already been reported by H. J. and N. W. Krase and V. L. Gaddy (9, 10). These workers have

noted increased yields of urea with increasing temperatures, with increasing weight-volume ratios and with increasing excesses of ammonia. They have also shown that an excess of carbon dioxide exerts little effect on the equilibrium, while an excess of water definitely reduces the yield of urea.

Yakovkin (17) was the first to report studies on this system at temperatures above 150° C. His work was carried out in lead-lined reactors and at relatively high weight-volume ratios. However, his procedure did not permit an accurate temperature measurement or insure that the equilibrium measured corresponded to the observed temperature range. Neumann and Sonntag (15) in 1931 reported yields of urea obtained by heating ammonium carbamate in a tin-lined reactor for varying periods of time. These authors¹ used a weight-volume ratio of 0.75 to 0.90 gram per cc. at temperatures from 135° to 155° C.

In the experimental development of a continuous process for the synthesis of urea from ammonia and carbon dioxide (4, 8, 10), it was essential to know the conditions most favorable for the transformation of ammonium carbamate into urea. With few exceptions the available data on the equilibrium yields of urea do not extend above 150° C. The majority of these previous determinations have been made at low weight-volume ratios ranging from 0.1 to 0.5 gram per cc. The purpose of this paper is to present the results obtained in such an investigation of the effect of temperature over the range 135° to 200° C. at higher weight-volume ratios than formerly used, and of the effect of the weight-volume ratio at 170° C. on the equilibrium yields of urea obtainable from ammonium carbamate. The results of previous investigators where the system studied consisted initially either of pure dry carbamate or of urea and water in the molecular ratio required to form carbamate have been given in Table I. It has been necessary in many cases to

¹ Information relative to the charging density employed was contained in a private communication from B. Neumann.

calculate the weight-volume ratio from the approximate volume of the containers as reported in the original papers.

PREPARATION OF MATERIALS

The ammonium carbamate was freshly prepared from anhydrous liquid ammonia and carbon dioxide. A weighed amount of liquid ammonia, about 70 grams, was transferred by means of refrigeration from a small steel pipet to a closed, wide-mouth reactor containing a close-fitting glass test tube. Both pipet and reactor were equipped with inlet and outlet valves. Carbon dioxide in excess of that required was then permitted to enter the cold reactor by direct connection with a cylinder of anhydrous carbon dioxide. Approximately 775 calories per gram of ammonia are liberated during this reaction. When the reactor had cooled, the excess carbon dioxide was released and the glass tube containing the carbamate in a solid compact mass was quickly removed and transferred to a vacuum desiccator. The carbamate was kept in this desiccator under slightly less than atmospheric pressure from 10 to 24 hours to insure removal of any occluded carbon dioxide. At the end of this period the hard lumps of carbamate had disintegrated owing both to the escape of the occluded carbon dioxide and to the partial vaporization of the carbamate. This material was considered to be pure carbamate inasmuch as it was found by analysis

to contain 35.74 per cent nitrogen compared to a theoretical content of 35.89 per cent.

The urea was prepared by purification of a thick urea liquor containing 35 to 40 per cent urea by weight that was available from previous operation of the experimental urea synthesis plant. After a period of sedimentation had precipitated the major portion of the metallic corrosion products, the supernatant liquid was decanted and subjected to decolorization by the admixture of bone charcoal followed by filtration. When a clear or only faintly straw-colored solution had been obtained, small fractions of the urea content were removed by quick chilling of the solution a few degrees below its saturation temperature. Repetition of this procedure on succeeding batches yielded quantities of urea which were further fractionated in like manner after solution in distilled water. The final product was dried in an air oven whose temperature was gradually raised to 50° C. This air-dried material was considered to be pure urea, since it was found by analysis to contain 20.08 per cent carbon, 6.72 hydrogen, and 46.60 nitrogen compared to a theoretical composition of 19.98 per cent carbon, 6.71 hydrogen, and 46.60 per cent nitrogen.

EXPERIMENTAL PROCEDURE

The new experiments reported fall into two series. The first series comprises those experiments in which equilibrium

TABLE I. YIELDS OF UREA OBTAINED BY PREVIOUS INVESTIGATORS ON THE SYSTEM UREA-WATER-AMMONIUM CARBAMATE

TEMP. ° C.	TIME Hours	INITIAL MATERIAL	CONTAINER	WEIGHT- VOL. RATIO Gram/cc	YIELD OF UREA %	OBSERVER	TEMP. ° C.	TIME Hours	INITIAL MATERIAL	CONTAINER	WEIGHT- VOL. RATIO Gram/cc.	YIELD OF UREA %	OBSERVER	
100	24	Carbamate	Tin	0.12	0.14	(6)	140	3	Carbamate	Tin	0.84	0.92	(15)	
	46	Carbamate	Glass	0.22	2.51	(10)		1	Carbamate	Glass	0.5	2.5	(12-14)	
	23	Carbamate	Glass	0.65	16.15	(10)		4.5	Carbamate	Tin	0.89	4.66	(15)	
	20	Carbamate	Glass	0.50	21.10	(10)		2	Carbamate	Glass	0.5	9.3	(12-14)	
115	24	Carbamate	Tin	0.11	0.65	(5)		3	Carbamate	Glass	0.5	14.4	(12-14)	
120	24	Carbamate	Tin	0.11	5.20	(5)		6	Carbamate	Tin	0.84	18.20	(15)	
	48	Carbamate	Tin	0.11	8.75	(5)		6.3	Carbamate	Tin	0.91	23.06	(15)	
125	24	Carbamate	Tin	0.12	1.7	(6)		48	Carbamate	Tin	0.11	27.96	(5)	
	48	Carbamate	Glass	0.21	14.07	(10)		24	Carbamate	Tin	0.11	28.06	(5)	
	48	Carbamate	Glass	0.53	18.20	(10)		5	Carbamate	Glass	0.5	29.4	(12-14)	
	47	Carbamate	Glass	0.62	18.40	(10)		9	Carbamate	Glass	0.5	38.0	(12-14)	
	25	Carbamate	Glass	0.57	29.95	(10)		9	Carbamate	Tin	0.83	39.1	(15)	
	120	Carbamate	Tin	0.43	39.4	(6)		12	Carbamate	Tin	0.89	39.60	(15)	
130	4	Carbamate	Glass	0.5	1.0	(12-14)		16	Urea + H ₂ O	Glass	0.5	39.8	(12-14)	
	5	Carbamate	Glass	0.5	1.62	(12-14)		16	Carbamate	Glass	0.5	40.6	(12-14)	
	8	Carbamate	Glass	0.5	2.3	(12-14)		24	Carbamate	Glass	0.5	41.11	(12-14)	
	10	Carbamate	Glass	0.5	4.2	(12-14)		40	Carbamate	Glass	0.5	41.3	(12-14)	
	12	Carbamate	Glass	0.5	6.27	(12-14)		39	Carbamate	Glass	0.5	41.4	(12-14)	
	18	Carbamate	Tin	0.05	9.50	(5)	145	2	Carbamate	Tin	0.76	1.77	(15)	
	16	Carbamate	Tin	0.07	11.34	(5)		0.5	Carbamate	Glass	0.16	6.0	(10)	
	16	Carbamate	Glass	0.5	13.6	(12-14)		3	Carbamate	Tin	0.90	8.00	(15)	
	16	Carbamate	Glass	0.5	13.7	(12-14)		1	Carbamate	Glass	0.5	14.3	(12-14)	
	21	Carbamate	Glass	0.5	25.1	(12-14)		1	Carbamate	Glass	0.15	15.83	(10)	
	18	Carbamate	Tin	0.07	27.06	(5)		2	Carbamate	Glass	0.19	20.85	(10)	
	48	Carbamate	Tin	0.08	27.2	(5)		1.5	Carbamate	Glass	0.24	21.80	(10)	
	24	Carbamate	Tin	0.11	28.18	(5)		5	Carbamate	Glass	0.5	25.2	(12-14)	
	48	Carbamate	Tin	0.11	30.06	(5)		5	Carbamate	Tin	0.88	32.70	(15)	
	24	Carbamate	Glass	0.5	33.56	(12-14)		3	Carbamate	Glass	0.5	36.9	(12-14)	
	26	Carbamate	Glass	0.5	36.6	(12-14)		5	Carbamate	Glass	0.5	42.3	(12-14)	
	39	Carbamate	Glass	0.5	39.2	(12-14)		5	Carbamate	Glass	0.36	42.4	(12-14)	
	39	Urea + H ₂ O	Glass	0.5	39.4	(12-14)		15	Carbamate	Tin	0.76	42.43	(15)	
134	3	Carbamate	Glass	0.5	3.01	(12-14)		15	Carbamate	Glass	0.37	42.5	(12-14)	
	5	Carbamate	Glass	0.5	8.12	(12-14)		10	Carbamate	Glass	0.5	42.7	(12-14)	
	13	Carbamate	Glass	0.5	27.6	(12-14)		16	Carbamate	Glass	0.5	42.8	(12-14)	
	19	Carbamate	Glass	0.5	38.2	(12-14)		24	Urea + H ₂ O	Glass	0.5	43.1	(12-14)	
	40	Carbamate	Glass	0.5	39.4	(12-14)		24	Carbamate	Glass	0.5	43.3	(12-14)	
	40	Carbamate	Glass	0.5	39.7	(12-14)		24	Carbamate	Glass	0.66	43.3	(12-14)	
	40	Carbamate	Glass	0.5	39.92	(12-14)		150	1	Carbamate	Tin	0.84	1.05	(15)
135	24	Carbamate	Tin	0.03	trace	(5)		24	Carbamate	Tin	0.11	24.28	(5)	
	6	Carbamate	Tin	0.75	1.26	(15)		2.33	Carbamate	Tin	0.78	26.6	(16)	
	8.25	Carbamate	Tin	0.82	3.84	(15)		2	Carbamate	Glass	0.36	32.08	(12-14)	
	18	Carbamate	Tin	0.08	10.2	(6)		2	Carbamate	Glass	0.40	32.48	(12-14)	
	18	Carbamate	Tin	0.08	13.3	(6)		2	Carbamate	Tin	0.39	33.5	(10)	
	24	Carbamate	Tin	0.05	13.6	(5)		2.33	Carbamate	Tin	0.75	36.9	(16)	
	1.75	Carbamate	Glass	0.37	17.25	(10)		4	Carbamate	Glass	0.39	43.0	(12-14)	
	42	Carbamate	Glass	0.20	22.20	(10)		3	Carbamate	Tin	0.49	44.09	(10)	
	10.5	Carbamate	Tin	0.75	25.00	(15)		3.5	Carbamate	Tin	0.75	44.4	(16)	
	24	Carbamate	Glass	0.08	28.0	(10)		4	Carbamate	Glass	0.49	44.57	(12-14)	
	24	Carbamate	Glass	0.11	30.07	(10)		151-152	21.5	Carbamate	Rezistal No. 4	0.69	28.0	(16)
	48	Carbamate	Tin	0.11	31.20	(5)		24	Carbamate	Rezistal No. 4	0.41	34.5	(16)	
	12.75	Carbamate	Tin	0.83	31.80	(15)		155	1	Carbamate	Tin	0.84	1.05	(15)
	25	Carbamate	Glass	0.32	32.10	(10)		2	Carbamate	Tin	0.80	23.17	(15)	
	22	Carbamate	Glass	0.32	33.85	(10)		3	Carbamate	Tin	0.84	43.90	(15)	
	24	Carbamate	Tin	0.12	35.5	(6)		9	Carbamate	Tin	0.83	44.44	(15)	
	48	Carbamate	Tin	0.22	36.6	(5)		8	Carbamate	Lead	0.90	27.0	(16)	
	48	Carbamate	Tin	0.43	36.7	(5)		8	Carbamate	Lead	0.95	39.0	(16)	
	18	Carbamate	Tin	0.89	38.60	(15)		8	Carbamate	Lead	0.74	43.3	(16)	
	18	Urea + H ₂ O	Glass	0.39	39.8	(12-14)		8	Carbamate	Lead	0.73	41.0	(16)	
	72	Carbamate	Tin	0.43	40.0	(5)	150-160	8	Carbamate	Lead	0.90	27.0	(16)	
	96	Carbamate	Glass	0.65	40.6	(12-14)	160-165	8	Carbamate	Lead	0.95	39.0	(16)	
	96	Carbamate	Tin	0.65	40.64	(5)	165-170	8	Carbamate	Lead	0.74	43.3	(16)	
	28	Carbamate	Tin	0.79	40.70	(15)	170-185	8	Carbamate	Lead	0.73	41.0	(16)	

was approached from both sides of the reaction, and the second series, those experiments in which equilibrium was approached only from the urea-water side.

The first series of experiments was carried out in the same Rezistal No. 4 reactors that were used by Krase and Gaddy (9) in their determination of the effect of an excess of ammonia on the carbamate-urea-water equilibria. The volumes of these reactors were 100 and 105 cc., respectively. The weight-volume ratio chosen was 0.9 gram per cc. Small amounts of carbamate were alternately charged to the reactor and compressed by the application of a compressive force of about 35 kg. per sq. cm. (500 pounds per square inch) until the reactor was filled within

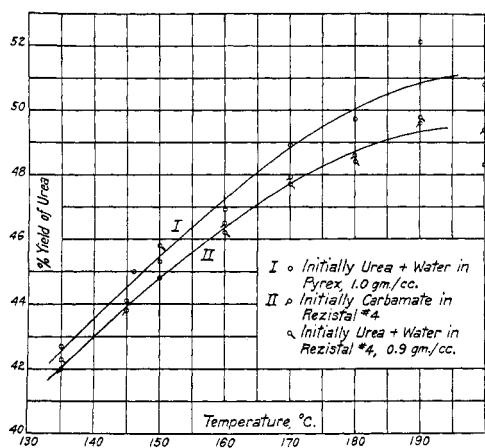


FIGURE 1. EFFECT OF TEMPERATURE ON EQUILIBRIUM YIELD OF UREA

4 mm. of the top. The reactor was closed and then weighed to determine the amount of carbamate charged. The loss in weight of the original containing vessel offered a check on this amount, which usually agreed within 0.5 to 0.75 gram. From the known weight-volume ratio of the carbamate charge, the equivalent weights of urea and water to produce the same weight-volume ratio were charged into the other reactor. It was not necessary to resort to compression in order to charge with urea and water. After the reactors were charged and securely closed to prevent loss of material by leakage, they were immersed in a thermostated oil bath capable of being maintained within $\pm 0.5^\circ\text{C}$. of the desired temperature. The period of heating at the lower temperatures was in most cases 24 hours; at a few of the higher temperatures this was shortened to 17 hours. These heating periods apparently were sufficient for the establishment of equilibrium under the temperature conditions of the experiments. At the end of the period of equilibration, the reactors were removed from the oil bath, freed of excess oil, and immediately immersed in cold water to chill the system quickly to temperatures at which the reaction rate is known to be inappreciable. It is assumed that because of this rapid cooling the conversion found actually corresponds to the composition existing at the temperature of equilibration. In all cases a residual pressure remained after the reactor had been returned to room

temperature. This fact had previously been noted at this laboratory and attributed to hydrogen derived from corrosion and ammonia cracking, since the gas was found to be combustible. In the first experiments this gas was released slowly through water to determine if it contained appreciable quantities of ammonia. Analysis of these solutions showed no measurable amount of ammonia; this procedure was therefore discontinued. The residual solid phase was dissolved in distilled water. Aliquot portions were taken for determination of the total nitrogen by the Kjeldahl method and of the ammonia nitrogen by titration.

The difference between the total nitrogen and the ammonia nitrogen was considered as urea nitrogen. The ratio of the urea nitrogen to the total nitrogen measured the fractional yield. The nitrogen found by analysis ranged from 98.5 to 99 per cent of that originally charged.

The object of the second series of experiments was to investigate the equilibrium in a more corrosion-resistant container than Rezistal No. 4 and at a higher weight-volume ratio. The weight-volume ratio chosen was 1.0 gram per cc., which necessitated limiting the experiments to an approach to equilibrium from the urea-water side. This seemed justified in view of the agreement reached in the first series. At 170°C . the second series was extended to cover the weight-volume ratio range from 0.2 to 1.0 gram per cc. These experiments were carried out in Pyrex glass tubes. Originally these tubes, closed at one end, were 12 mm. o. d., 9 mm. i. d., and 12 cm. long. About 5 cm. from the open end they were constricted to 6 mm. o. d. and 3 mm. i. d. The volume of these tubes below the constriction ranged from 3.5 to 4.2 cc. They were carefully calibrated to 0.01 cc. The closest approach of the material to the constricted neck of the tube was approximately 2 cm.

These tubes, after being chilled in an ice and brine mixture, were quickly sealed off at the constriction with a small oxy-hydrogen flame. They were then placed singly in the Rezistal No. 4 reactors used in the preceding experiments and surrounded by a mixture of urea and water in molecular proportions and at a weight-volume ratio between 0.9 and 1.0 in order to equalize the pressure within and outside the glass tubes. The reactors were then subjected to the same treatment as in series 1. After completion of the equilibration, etc., the glass tubes were removed, washed, and dried preparatory to opening for analysis. Initial attempts to open the tubes under water with a file were unsuccessful since the force with which the tips were liberated caused loss of the solution. Later several tubes exploded spontaneously after having been held at room temperature for several hours. Through the courtesy of R. O. E. Davis and co-workers of this laboratory an apparatus, devised by them, was made available for crushing these tubes without loss of the contents. This apparatus permitted chilling the tubes in liquid air before crushing them under water by longitudinal compression. The solution obtained by dissolving the solid phase was freed of broken glass by filtration and prepared for analysis as in series 1.

The percentage nitrogen lost in these experiments was approximately the same (1 to 1.5 per cent) as in the first series. The equilibrium yield of urea was determined in this series over

TABLE II. EXPERIMENTAL YIELDS OF UREA

(Equilibrium approached from both sides of the reaction in Rezistal No. 4 reactors at 135° to 200°C .)

EXPERIMENT	TEMP. $^\circ\text{C}$.	TIME Hours	INITIAL MATERIAL	WEIGHT-VOL. RATIO Gram/cc.	YIELD OF UREA		EXPERIMENT	TEMP. $^\circ\text{C}$.	TIME Hours	INITIAL MATERIAL	WEIGHT-VOL. RATIO Gram/cc.	YIELD OF UREA	
					%	AVERAGE %						%	AVERAGE %
24	135.0	26	Urea + H ₂ O	0.90	42.4		5a	170.0	24	Carbamate	0.97	47.9	
25	135.0	26	Urea + H ₂ O	0.90	42.2	42.3	6a	170.0	24	Carbamate	0.94	47.8	47.9
24a	135.0	26	Carbamate	0.90	41.8		7	180.0	24	Urea + H ₂ O	0.92	48.3	
25a	135.0	26	Carbamate	0.90	42.2	42.0	8	180.0	24	Urea + H ₂ O	0.90	48.5	48.4
26	145.0	24	Urea + H ₂ O	0.90	44.1		7a	180.0	24	Carbamate	0.96	48.8	
27	145.0	24	Urea + H ₂ O	0.90	44.0	44.1	8a	180.0	24	Carbamate	0.95	48.4	48.6
26a	145.0	24	Carbamate	0.90	43.8		9	190.0	24	Urea + H ₂ O	0.92	51.2	
27a	145.0	24	Carbamate	0.90	43.7	43.8	10	190.0	24	Urea + H ₂ O	0.92	48.2	
1	150.0	24	Urea + H ₂ O	0.38	42.0	42.0	14	190.0	17	Urea + H ₂ O	0.92	49.5	
1a	150.0	24	Carbamate	0.40	42.0	42.0	15	190.0	4	Urea + H ₂ O	0.92	50.2	49.8
2	150.0	24	Urea + H ₂ O	0.90	45.8	45.8	9a	190.0	24	Carbamate	0.97	49.0	
2a	150.0	24	Carbamate	0.95	44.8	44.8	10a	190.0	24	Carbamate	0.97	49.1	
3	160.0	24	Urea + H ₂ O	0.90	46.4	46.2	14a	190.0	17	Carbamate	0.97	50.1	
4	160.0	24	Urea + H ₂ O	0.96	45.9	46.2	15a	190.0	4	Carbamate	0.97	50.0	49.6
3a	160.0	24	Carbamate	1.01	46.4		11a	200.0	24	Urea + H ₂ O	0.97	48.4	
4a	160.0	24	Carbamate	1.01	46.5	46.5	12	200.0	24	Urea + H ₂ O	0.92	48.1	
5	170.0	24	Urea + H ₂ O	0.92	47.9	47.7	13	200.0	17	Urea + H ₂ O	0.92	48.7	48.4
6	170.0	24	Urea + H ₂ O	0.90	47.5	47.7	12a	200.0	24	Carbamate	0.96	49.2	
							13a	200.0	17	Carbamate	0.96	49.5	49.4

the temperature range 135° to 200° C. at a weight-volume loading ratio of one gram per cc. In addition, at 170° C. the equilibrium yield was determined at weight-volume ratios between 0.2 and 0.8 gram per cc.

EFFECT OF TEMPERATURE ON THE EQUILIBRIUM YIELD OF UREA

EXPERIMENTS IN REZISTAL NO. 4 REACTORS. The yields of urea obtained in the first series of experiments carried out in Rezistal No. 4 reactors over the temperature range 135° to 200° C. in which equilibrium was approached from both sides of the reaction at a weight-volume ratio of 0.9 gram per cc., ranged from 42.0 per cent at 135° C. to 49.5 at 190° C. The data for these experiments are given in Table II and represented graphically in Figure 1 (curve I). The yield of urea increases with increasing temperatures with the appearance of an apparent maximum at about 190° C.

EXPERIMENTS IN PYREX GLASS TUBES. The second series of experiments in which equilibrium was approached only from the urea-water side in Pyrex glass tubes, at the higher weight-volume ratio of 1.0 gram per cc., showed yields of urea ranging from 42.7 per cent at 135° C. to 52.1 at 190° C. The results of these experiments are given in Table III and Figure 1 (curve II).

TABLE III. EXPERIMENTAL YIELDS OF UREA

(Equilibrium approached from urea-water side of reaction in sealed glass tubes at 135° to 200° C.; weight-volume ratio = one gram per cc.)

EXPERIMENT	TEMP. ° C.	TIME Hours	YIELD OF UREA	
			%	AVERAGE %
29	135.0	48	43.0	
29a	135.0	48	42.3	42.7
30	146.0	24	44.4	
30a	146.0	24	45.5	45.0
31	150.0	24	45.3	
31a	150.0	24	45.2	45.3
32	160.0	24	47.0	
32a	160.0	24	46.8	46.9
34	170.0	24	48.8	
34a	170.0	24	48.9	48.9
39	180.0	24	50.0	
39a	180.0	24	49.4	49.7
40	190.0	17	51.5	
40a	190.0	17	52.6	52.1
41	200.0	20	50.3	
41a	200.0	20	51.2	50.8

EFFECT OF WEIGHT-VOLUME RATIO ON EQUILIBRIUM YIELD OF UREA

Krase and Gaddy (10) obtained increased yields of urea with increasing weight-volume ratios up to 0.6 gram per cc. at 150° C. The present experimental data presented in Table IV and Figure 2 confirm this for weight-volume ratios up to 1.0 gram per cc. at 170° C. Yields of urea of 34.5 and 49.0 per cent were obtained for weight-volume ratios of 0.2 and 1.0 gram per cc., respectively. A plot of the yield of urea against the reciprocal of the weight-volume ratio (Figure 2, curve II) shows that within the range of the experiments the urea yield is a linear function of this reciprocal.

TABLE IV. EXPERIMENTAL YIELDS OF UREA

(Equilibrium approached from urea-water side of reaction in sealed glass tubes at 170° C.; time 24 hours)

EXPERIMENT	WEIGHT-VOL. RATIO Gram/cc.	YIELD OF UREA	
		%	AVERAGE %
35	0.20	33.5	
35a	0.20	35.5	34.5
36	0.40	43.1	
36a	0.40	42.7	42.9
37	0.60	46.4	
37a	0.60	46.5	46.5
38	0.80	48.2	
38a	0.80	48.3	48.3
34	1.00	48.9	
34a	1.00	48.9	48.9

DISCUSSION AND COMPARISON OF RESULTS

The new experiments show increasing conversion of ammonium carbamate into urea with temperature up to an apparent maximum at about 190° C. The corrosive action of this system toward ordinary materials of construction is considerable at 150° to 160° C. and increases rapidly at higher temperatures. 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.

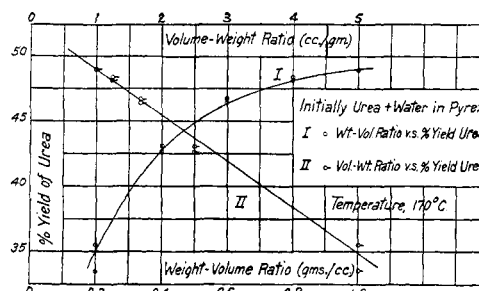


FIGURE 2. EFFECT OF WEIGHT-VOLUME RATIO ON EQUILIBRIUM YIELD OF UREA

The results of the present work at the high weight-volume ratios of 0.9 in Rezistal No. 4 reactors and 1.0 in Pyrex tubes supply experimental confirmation of the conclusion of Matignon and Frejacques (12) that greater yields of urea were to be expected at the higher weight-volume ratios. In every case the yields of urea obtained at a given temperature are in excess of those previously reported. The following comparison illustrates this point over the temperature range 135° to 150° C.:

TEMP. ° C.	WEIGHT-VOL. RATIO Gram/cc.	CONTAINER	YIELD OF UREA	OBSERVERS
			%	
135	0.65	Tin	40.64	(5)
	0.79	Tin	40.70	(15)
	0.90	Rezistal No. 4	42.2	Present authors
145	1.00	Pyrex	43.7	Present authors
	0.66	Glass	43.3	(12)
	0.76	Tin	42.43	(15)
	0.90	Rezistal No. 4	43.7	Present authors
150	1.00	Pyrex	45.0	Present authors
	0.38	Pyrex	41.9	Present authors
	0.49	Glass	44.6	(14)
	0.92	Rezistal No. 4	45.3	Present authors
	1.00	Pyrex	45.3	Present authors

The work of Yakovkin (17) over the range 150° to 185° C. is omitted from this comparison since his procedure of allowing the equilibrated mixture to cool in place in the heating bath precluded any exact knowledge of the temperature corresponding to the yield of urea found.

At 170° C. the yields of urea obtained at weight-volume ratios of 0.2 and 1.0 gram per cc. were 34.5 and 49.0 per cent, respectively. This is a 42.0 per cent increase in conversion for a 400 per cent increase in the weight-volume ratio. The curves of Figure 2 show that only slight additional increases in conversion are to be expected at higher weight-volume ratios than 1.0 gram per cc. Extrapolation of the empirical curve 2 of Figure 2 to volume-weight ratios corresponding to the approximate density of the liquid phase indicates a probable conversion of 50.3 per cent which is a 2.7 per cent increase over that experimentally found.

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Effect of Temperature on Tensile Properties of Vulcanized Rubber

A. A. SOMERVILLE AND W. F. RUSSELL, R. T. Vanderbilt Company, Inc., New York, N. Y.

THE amount of published data on the physical properties of vulcanized rubber at widely different temperatures is meager considering the wide range of temperatures over which rubber products are expected to give service. Temperature variations due to seasonal causes alone are large, but these may be greatly accentuated in rubber articles such as tires, tubes, fan belts, and motor mounts, by severe conditions of service. An understanding of the behavior of vulcanized rubber at widely different temperatures, and particularly at high temperatures, is therefore becoming more and more essential for the development of suitable compounds for rubber particles that must withstand large temperature variations.

PREVIOUS WORK

A report in 1926 by van Rossem and van der Meijden (3) on the influence of high temperatures on the stress-strain curve of vulcanized rubber was the first systematic attack upon this problem. These investigators did not use commercial compounds but a pure gum mix (92.5 rubber, 7.5 sulfur by weight). Tests were made at temperatures from 24° to 147° C. It was found that, as the temperature increased, the stress-strain curve shifted progressively toward the elongation axis—i. e., the rubber softened; that the amount of shift was further influenced by the degree of vulcanization and the time of heating; that the tensile strength reached a maximum at about 70° C. and then decreased; that higher temperatures imparted brittleness to the rubber, which disappeared on cooling—i. e., was not apparent in room temperature tests; and that the brittleness appeared in cures with high vulcanization coefficients sooner than in those with low coefficients. The authors suggested that high-temperature testing might be considered as a method of artificial aging. A further communication in 1927 by the same authors (4) deals with changes in the stress-strain curve, hardness, and plasticity of vulcanized rubber heated up to 147° C.

Breuil (1) in 1910 gave data on four compounds (including ebonite) over a range of -10° to +100° C. Le Blanc and

The tensile properties and tear resistance of a large number of commercial inner tubes, before and after aging by different methods, are studied at 0°, 25°, and 100° C. A number of uncured bus-truck tube stocks are also studied from the point of view of their capacity to withstand high temperatures.

The effect of testing rubber at 100° C. as compared with room temperature is discussed; how some compounds collapse at 100° C., while others have tensile properties equal to, or better than those at 25°, is shown. The effect of testing artificially aged specimens at 100° C., as well as at 25° C., is discussed; the high-temperature test may reveal conditions of deterioration and overcure that are not noticeable in the 25° tests. The compounding and curing conditions that lead to high tensile properties at 100° C., as well as those which cause inferior quality, are discussed.

Kroeger (2) in 1926 gave some data on the effect of low temperatures, chiefly on rubber-sulfur mixes, and concluded that the presence of organic accelerators did not materially affect their results.

The U. S. Bureau of Standards (6) in 1928 published data giving physical tests on six different types of rubber compounds at temperatures from -70° to +147° C. The results showed that at very low temperatures the specimens became rigid, with greatly increased tensile strength which gradually decreased with rising temperature until, at 147° C., it became practically negligible. All six compounds showed the same type of behavior, and it was concluded that the differences due to compounding ingredients were differences in degree rather than in kind.

In 1928 Somerville and Cope (5) published results on the effect of temperature on the stress-strain properties of several different types of laboratory compounds. It was shown that wide variations appeared in the stress-strain curves of the same stock at different temperatures; that there was a progressive drop in the stress values as the temperature was raised from 0° to 100° C.; that the amount of sulfur used was a factor in the stress-strain relationship at different temperatures; that the stress-strain properties at different temperatures varied for different rubbers; that the state of cure caused a wide variation in tests at different temperatures; that successive stretchings of the same specimen caused large decreases in the stress after the first or second cycle; that stripping tests on frictions showed much lower strength at 100° than at 0° C.; and that overcures were indicated prominently at 100° C. by shortness and low tensile, whereas at room temperatures this shortness might remain concealed.

These results were limited by the dimensions of the temperature control chamber attached to the testing machine, which permitted tests only up to 500 per cent elongation. Since then the tester has been equipped with a 48-inch tank which allows test pieces to be stretched at the desired temperature to rupture, so that complete stress-strain data and ultimate tensiles can be obtained.