The Review of Physical Chemistry of Japan Vol. 21 No. 1 (1950)

EQUILIBRIUM OF UREA—WATER SYSTEM, II.

The relation between equilibrium pressure and packing ratio, analysis of gas phase and corrosion of nickel-chrome steel.

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Introduction.

It was reported in the previous paper that the equilibrium pressure is changed by packing ratio. For the purpose of explaining this relation, the author measured the equilibrium pressure at the packing ratios of 0.1, 0.3, 0.5 and 0.7 g/cc and at the temperatures of 150, 170, 190 and 210°C. To the gas phase at those temperatures are performed the gas analysis and measuring of ammonia and urea for the condensed solid after cooling. As the equilibrium pressure is changed by the volume of liquid phase, the pressure will change in the case of excess water. The equilibrium pressures are measured in this case at the packing ratios of 0.2, 0.3, 0.4, 0.5, and 0.6 g/cc. Moreover, the residual urea at each packing ratios of 0.075, 0.05 and 0.025 g/cc is measured. As to the corrosion of autoclave material by urea synthesis, Thompson, Krase and Clark¹⁾ reported that the silicon rich steel is suited for urea synthesis from the expriements for nickel-chrome-silicon steel at a temperature of 140°C, but the corrosion of nickel-chrome steel added manganese, molybdenum, silicon, titanium and copper is reported in this paper.

Apparatus.

The reaction vessel and the pressure measuring part are of quite the same construction as in the previous paper. In this case, steel pipe (length 100 mm, O.D 10 mm, I.D 5 mm), is fitted with two high pressure valves between the reaction vessel and the pressure gauge. The vessel (c) is the same in the previous paper and packings of valves are constructed with silver plate and lead. The total volume of the reaction vessel is 29.4 cc and the volume of the cut part of steel pipe is 3.15 cc. The apparatus in the case of excess water is all the same as the previous paper and that in the experiments of packing ratio smaller than 0.1 is used a nickel-chrome steel vessel 18.2 cc. For the test of corrosion,

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1) I. G. Thomson, H. J. Krase and K. G. Clark, *Ind. Eng. Chem.*, 22, 735 (1930)

the pressure gauge is omitted to avoid the influence of mercury for sealing. After the air is pumped out, the calculated water is added. The test piece* is of a cube of 5 mm and for avoiding the contact with neighbouring piece, each piece is inserted in a glass tube.

Experimental.

For simplifing the apparatus, in the case of gas phase analysis, the air in the reaction vessel is not pumped out. The calculated urea and water are sealed, 3 hours after reaching the desired temperature, cutted the two valves, and cooled in ice water. The gas phase in cooling is analysed after dissolving in water. Added 5 % potassium hydroxide solution in this solution, bubbled the air for 2 hours at 40°C and evolved ammonia is caught by the standard sulfuric acid solution. After this procedure is over, the amount of urea is measured by the method of Kjehldahl.

Experimental results.

(I) Pressure change by packing ratio and analysis of gas phase at elevated temperatures.

The equilibrium pressure (Fig. 1), carbon dioxide in gas phase after cooling (Fig. 2), ammonia (Fig. 3) and urea (Fig. 4) in condensed solid after cooling, and residual urea (Fig. 5) in the reaction vessel are measured for the experiments of temperatures 150, 170, 190, 210°C, packing ratios of 0.1, 0,3, 0.5, 0.7 g/cc. These results are illustrated in Table 1.

(II) The pressure change of various mol-ratio of urea-water.

The equilibrium pressure is measured for the experiments

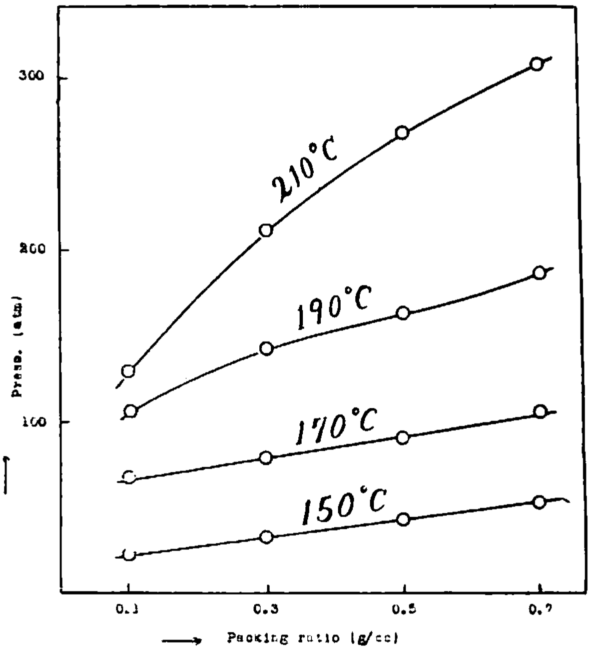

Fig. 1 Equilibrium pressure—packing ratio curves.

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* Samples from Nippon Metal Industry Co., Kawasaki.

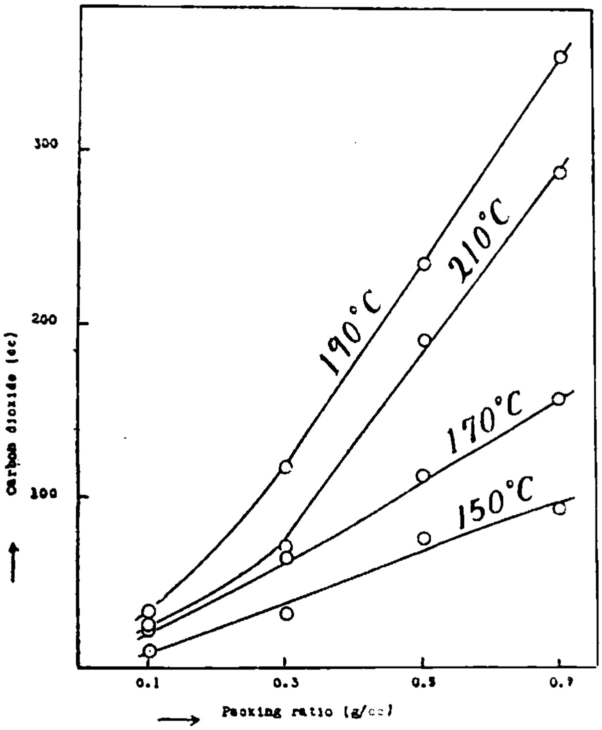

Fig. 2 Carbon dioxide in gas phase—packing ratio curves.

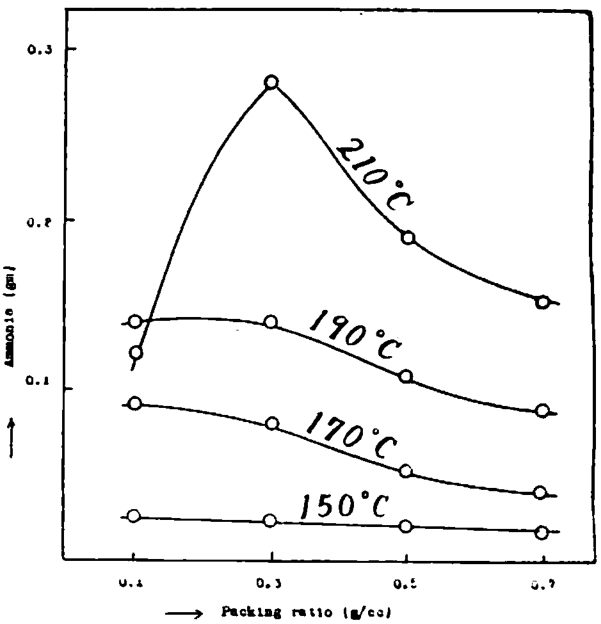

Fig. 3 Gas phase ammonia in condensed solid—packing ratio curves.

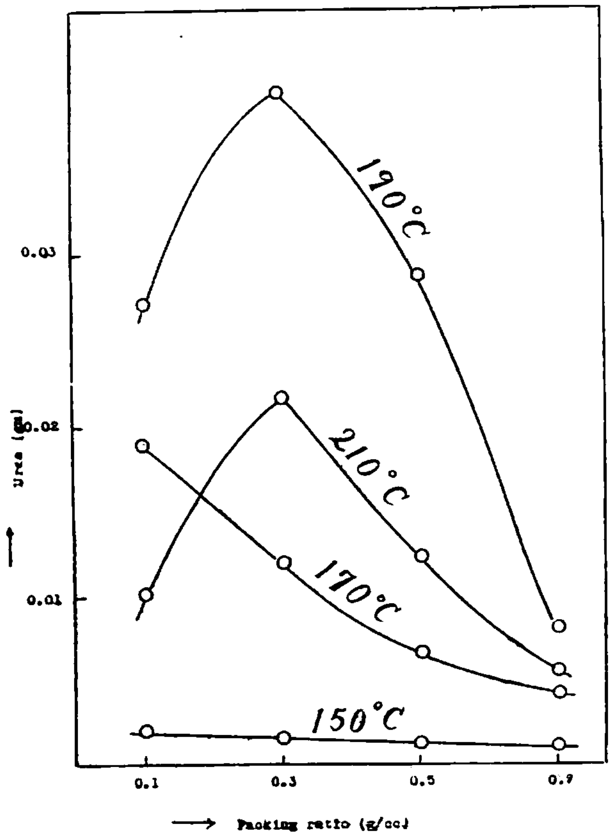

Fig. 4 Gas phase urea in condensed solid—packing ratio curves.

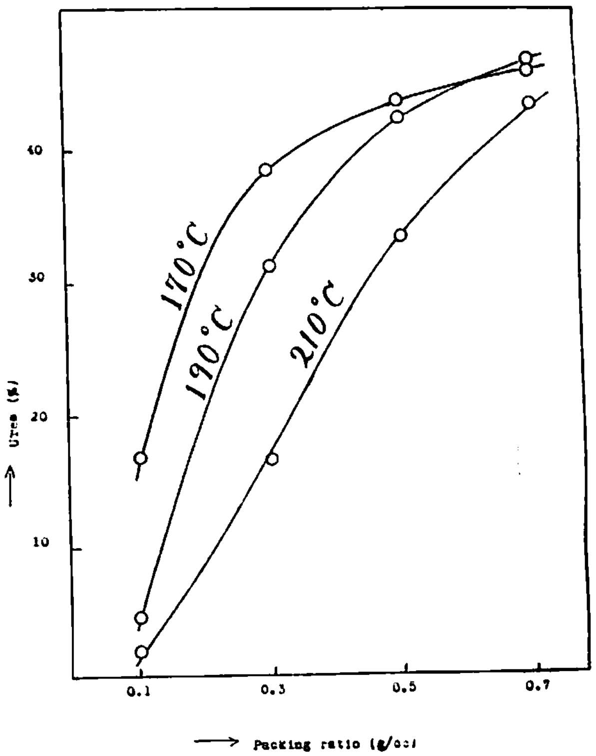

Fig. 5 Residual urea in reaction vessel—packing ratio curves.

Table 1

Temp.	Packing ratio,	Equil. press.	Gas phase					Liq. phase
			Gas			Condensed solid		Residual urea
°C	g/cc	atm.	Total cc	CO_2 cc	H_2 cc	Ammonia gm.	Urea gm.	%
210	0.1	130	28.9	20.1	8.8	0.1208	0.0101	1.9
,,	.3	212	78.1	68.7	9.4	.2794	.0216	16.1
,,	.5	268	197.7	190.9	6.8	.1884	.0123	33.2
,,	.7	306	295.8	286.6	9.2	.1515	.0056	43.1
190	.1	106	40.7	32.0	8.7	.1376	.0271	4.5
,,	.3	143	127.7	114.5	13.2	.1391	.0394	31.1
,,	.5	163	248.1	233.9	14.2	.1065	.0287	42.2
,,	.7	186	369.7	354.5	15.2	.0885	.0082	46.3
170	.1	68	31.4	22.9	8.5	.0929	.0088	16.7
,,	.3	78	71.4	64.2	7.2	.0803	.0119	38.4
,,	.5	90	116.0	111.5	4.5	.0523	.0067	43.3
,,	.7	105	159.6	156.0	3.6	.0404	.0044	45.5
150	.1	23	14.1	9.0	5.1	.0249	.0020	54.9
,,	.3	32	33.9	28.6	5.3	.0217	.0016	53.6
,,	.5	43	81 2	76.2	5.0	.0194	.0013	50.0
,,	.7	53	94.0	90.6	3.4	.0168	.0010	49.0
		Fig. 1		**Fig. 2**		**Fig. 3**	**Fig. 4**	**Fig. 5**

of 190°C, 3 hours, at various mol-ratios. These results are illustrated in Fig. 6.

(III) The residual urea in the reaction vessel is measured for the experiment of temperatures 190, 210, 230°C, packing ratios 0.075, 0.05, 0.025 g/cc

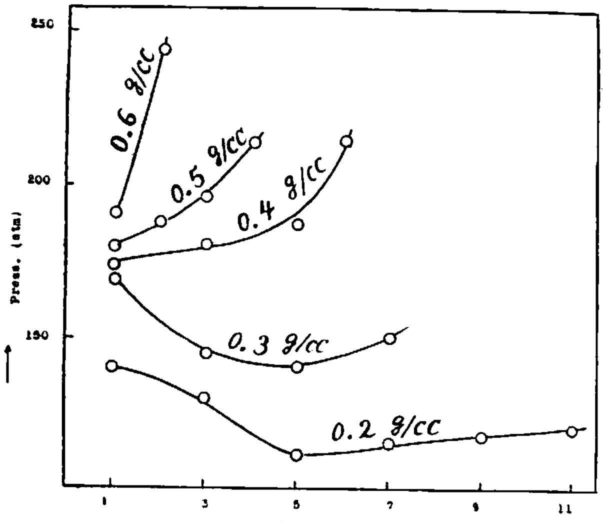

Fig. 6 Water/urea-equilibrium pressure curves at 190°C.

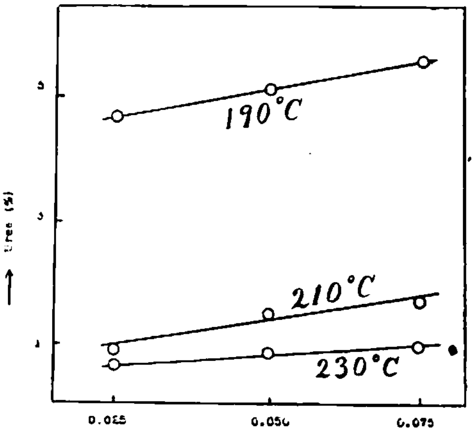

Fig. 7 Residual urea-packing ratio curves.

referring to 3 hours. These results are illustrated in Fig. 7.

(IV) Corrosion.

The test pieces in Table 2 are tested for 4 days at 170°C and calculated the weight loss per cm^2 from the decreasing of weight. The pressure will be about 100 atm/cm^2 as the packing ratio is 0.6 g/cc. These results are illustrated in Table 2.

Table 2

Sample No.	Percentage of elements								Decreased weight, mg/cm^2	
	C	Cr	Ni	Mo	Mn	Si	Ti	Cu	4 days	a day
1(Ag)									0.16	
2(Pb)									5.66	
3	0.15	24.5	3.0	2.0	0.6	0.6			22.57	
4	.10	18	10	2.0	0.6	0.6			3.22	
5	.1	16	12	2.5					4.59	
6	.1	16	14	2.5					5.94	
7	.07	16.5	12	2.8				1.8	16.46	
8	.1	25	3	2.5			1.2		0	
9	.18	24.65	3.4	3.64			0.34		0.30	
10	.15	19	22	1.0			0.05		0.70	
11	.21	25.3					0.01		0.13	
12	.07	30.59			0.34	0.66			15.23	
13	.08	28.38	4.45	2.35	0.5	0.72			1.63	
14	.09	23.24	3.22	2.50	0.5	0.94	0.10		2.84	
15	.08	23.14	2.87	2.42	0.5	0.77	0.32		0.71	
16	.09	27.40	3.40	2.20	0.5	0.60	0.69		0.10	
17	.06	9.08	17.71	7.42	1.04	0.55			2.48	
18	.06	18.99	11.17	2.10	1.41	0.55		1.73	3.59	
19	.10	24.5		2	0.5	0.5	0.5		0.09	
20	.10	24.5	1	2	0.5	0.5	0.5		0	
21	.10	24.5	2	2	0.5	0.5	0.5		0.09	
22	.08	23.14	2.87	2.42	0.56	0.77	0.32		0.67	
23	.19	14.76			0.32	0.40				168.5
24	.07	18.21			0.27	0.42				85.8
25	.15	25.62			0.33	0.55				84.4

Considerations.

(1) In the equilibrium experiments, there exists a residual pressure and the greater part of gas phase is carbon dioxide. It is a matter of course for the solubility of ammonia is greater than carbon dioxide. The ammonia in gas phase is decreased as the packing ratio is increased. This will explain that the dissolved ammonia is increased as the liquid phase is increased by increasing

packing ratio. On the other side, carbon dioxide in gas form included in condensed solid is increased as the packing ratio is increased. This will explain that the solubility of carbon dioxide to liquid phase is considerably small, and that consequently the increase of carbon dioxide in gas phase is greater than the increase of dissolved carbon dioxide as the packing ratio is increased. It is confirmed that the ratio of ammonia and carbon dioxide in condensed solid is 2 to 1 and therefore it will be ammonium carbamate. The decrease of the solubility of ammonia causes the increase of ammonia in gas phase as the temperature rises at the same packing ratio. The maximum of carbon dioxide in cooling is in 190°C, and the total carbon dioxide in gas phase increases as the temperature rises. In the previous paper, the equation of vapour pressure depends on packing ratio, and it will be explained by the fact that the equilibrium pressure is the vapour pressure of urea solution dissolved ammonia and carbon dioxide. But above 190°C, ammonia is smaller in the case of 0.1 g/cc than 0.3 g/cc, this is because that the absolute volume of liquid phase is small. The amount of urea in gas phase is largest at 190°C, this is the same tendency in the case that the residual urea in the reaction vessel is largest at the long run of the same temperature or the high packing ratio*. The volume of hydrogen is influenced by the wall of the reaction vessel and steel pipe, and because of the fresh vessel and valves, hydrogen evolved at 210°C is smaller than 190°C.

(II) In the case of excess water, the equilibrium pressure is measured for the experiment of various packing ratio of urea. It is anticipated that the equilibrium of $2NH_3+CO_2=H_2O+NH_2CONH_2$ is inclined to the left because that ammonia and carbon dioxide is increased as the water is increased. Ammonia in gas phase decreased as the liquid phase increased and carbon dioxide in gas phase increased when the increase of the total carbon dioxide was greater than dissolved carbon dioxide.

(III) In the case when the packing ratio is smaller than 0.1, the weight of water which corresponds to that of urea in Fig. 7 is smaller than steam density at that temperature: Consequently there exists no liquid phase at elevated temperature. For this reason, the equilibrium equation is inclined to the left as the temperature becomes higher, and the equilibrium pressure will be higher when packing ratio increases, so the equilibrium is inclined to the right when the pressure becomes higher.

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* cf. Fig. 3 in the previous paper.

(IV) As to corrosion, it will conclude from Table 2 that the corrosion decrease (a) as chrome increases in Cr—Mn—Si steel, (No. 23, 24, 25, 12) (b) as nickel and molybdenum exist in Cr—Mn—Si steel, (No. 12, 13) (c) as titanium increases in all cases and there is no influence of nickel in the case of 0.5% titanium. A Considerable amount of nickel is necessary for the zero percent titanium. (d) The corrosion increases in the existence of copper.

The author wishes to express his appreciation to Professor R. Kiyama for his valuable guidance during the course of this research and heaıty thanks to the Ministry of Education for the Scientific Research Grant.

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