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Phase Diagram of the System Urea + Hydrogen Peroxide + Water

Hong-Kun Zhao,* Bao-Zeng Ren, and Guo-Ji Liu

Institute of Chemical Engineering, Zhengzhou University,
Zhengzhou, He'Nan 450002, People's Republic of China

Hong-Xian Wang

Department of Chemistry, Nantong Teacher's College, Nantong, Jiangsu 226007, People's Republic of China

The phase diagram of the system urea + hydrogen peroxide + water was investigated at 273.15 K and 283.15 K, respectively, using the moist solid method. The solubilities of urea and hydrogen peroxide were determined. The formation of the compound $CO(NH_2)_2 \cdot H_2O_2$ was confirmed by phase-diagram studies, and the crystalline region of the adduct urea hydrogen peroxide was determined.

1. Introduction

Percarbamide, also named urea hydrogen peroxide with gross formula $CO(NH_2)_2 \cdot H_2O_2$, is an adduct of hydrogen peroxide with urea and is an important fine chemical used in several oxidation processes[1−6] as well as a safe source for the production of hydrogen peroxide.[7] Percarbamide has a high proportion of hydrogen peroxide (36 mass %) with an active oxygen content of 17.02 mass %.

The crystal structure of urea hydrogen peroxide 1:1 complexes was first experimentally investigated by X-ray[8] and later by neutron diffraction at low temperatures.[9,10] Results indicate that the unit cell is orthorhombic, *Ponca*, with $a = 6.86$, $b = 4.83$, $c = 12.92$ Å and $Z = 4$. The nitrogen atoms of the urea molecule make two hydrogen bonds to hold a hydrogen peroxide molecule in a face-to-face position, and the carbonyl oxygen forms hydrogen bonds to a pair of peroxide molecules. This generates four strings of hydrogen peroxide molecules: two parallel to *a*, but at an angle to *c*. According to existing literature,[11,12] the ternary phase diagram of the system sodium carbonate + hydrogen peroxide + water has been examined, but a limited study of the system urea + hydrogen peroxide + water has been made previously and the existence of the compound $CO(NH_2)_2 \cdot H_2O_2$ has been reported.[11] The experimental data are not sufficient to enable the phase diagram to be constructed. In this paper, we expand our studies on hydrogen peroxide to the urea hydrogen peroxide complexes. The goal of this work is to investigate the ternary phase diagram of the system urea + hydrogen peroxide + water at 273 K and 283.15 K by the moist solid method.

2. Experimental Section

To prepare the compound formed between urea and hydrogen peroxide, the following method has been used. A known mass of urea was dissolved in aqueous hydrogen peroxide of various concentrations (0−65 mass %), and the saturated solution was transferred to a conical flask. The conical flask was stoppered and placed in a thermostat at (273.15 ± 0.1) K or (283.15 ± 0.1) K. After 6 to 12 h, a sample of the liquid phase was analyzed, and this was repeated several hours later. If the two analyses gave identical results, it was assumed that equilibrium had been reached and the solid and the liquid phase were separated by filtration and analyzed. To avoid appreciable decomposition of hydrogen peroxide, the temperatures selected for the studies of the system were 273.15 K and 283.15 K.

Table 1. Solubilities of the System Urea + Hydrogen Peroxide + Water at 273.15 K[a]

liquid phase		moist solid phase		
$100w_1$	$100w_2$	$100w_1$	$100w_2$	solid phase
4.51	50.62	58.73	36.89	P
4.88	45.85	59.02	36.91	P
5.17	39.62	59.47	36.82	P
4.93	35.21	58.92	36.87	P
5.25	32.28	58.86	36.80	P
5.91	27.37	58.85	36.76	P
6.68	22.98	59.27	36.47	P
8.12	20.46	59.24	35.89	P
9.13	18.47	59.06	35.32	P
10.00	15.13	59.47	35.60	P
11.72	13.04	59.80	35.32	P
14.01	10.24	59.67	35.14	P
17.78	8.73	59.21	34.45	P
22.11	7.36	60.42	33.89	P
25.05	7.03	60.62	33.30	P
27.95	6.38	60.21	33.88	P
30.41	5.99	60.23	32.53	P
33.70	5.35	60.83	33.01	P
37.06	5.26	60.83	33.80	P
38.21	3.78	60.87	33.30	P
41.34	5.31	97.28	0.38	B
44.23	5.25	97.06	0.36	B
36.76	1.50	94.91	0.11	B

[a] P, $CO(NH_2)_2 \cdot H_2O_2$; B, $CO(NH_2)_2$; *w*, mass fraction.

Analysis. The moist solid samples were dissolved in water, and aliquot portions of the solutions so obtained and those of the liquid-phase samples were used for the analyses.

The active oxygen was determined by titrating the acidified solution with standard potassium permanganate. The urea was determined by the methanol method: concentrated sulfuric acid was added to the urea solution, converting the amine in urea to ammonium, and finally methanol was added to the ammonium solution. The

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* Corresponding author. Telephone: +1-86-371-3887503. Fax: +1-86-371-3887318. E-mail: hkzhao@zzu.edu.cn.

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Table 2. Solubilities of the System Urea + Hydrogen Peroxide + Water at 283.15 K[a]

liquid phase		moist solid phase		
$100w_1$	$100w_2$	$100w_1$	$100w_2$	solid phase
9.96	52.57	61.51	36.75	P
9.55	44.43	61.79	36.73	P
11.14	39.36	60.83	36.81	P
10.48	35.39	61.92	36.54	P
10.87	29.91	60.41	36.12	P
11.09	26.78	60.37	36.05	P
10.63	24.42	60.48	36.63	P
12.71	19.38	61.02	35.21	P
11.48	21.45	61.17	35.38	P
14.60	16.77	61.39	34.71	P
15.94	15.85	61.27	34.93	P
17.87	13.83	62.08	33.56	P
21.17	11.22	62.47	33.52	P
23.68	10.01	62.31	33.77	P
26.52	9.67	62.46	33.38	P
29.77	8.92	62.71	33.32	P
33.03	8.32	62.69	33.30	P
33.43	8.29	62.64	33.19	P
33.95	8.16	62.27	33.24	P
37.44	7.39	62.50	33.41	P
41.28	7.15	62.73	33.36	P
46.31	6.39	72.67	23.05	P + B
46.32	5.78	78.21	17.15	P + B
43.35	4.76	94.45	1.17	B
43.74	2.26	95.07	0.79	B

[a] P, $CO(NH_2)_2 \cdot H_2O_2$; B, $CO(NH_2)_2$; *w*, mass fraction.

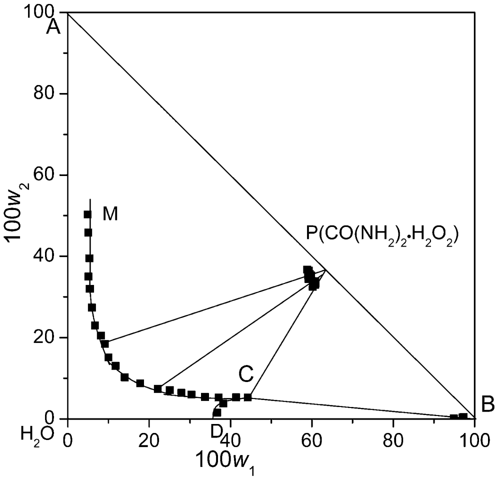

Figure 1. System urea (1) + hydrogen peroxide (2) + water (3) at 273.15 K: C, cosaturated point; P, $CO(NH_2)_2 \cdot H_2O_2$; A, H_2O_2; B, $CO(NH_2)_2$; D, solubility of $CO(NH_2)_2$ in water; M, experimental data.

ammonium was thus determined by titrating with standard sodium hydroxide.

The experimental results are given in Tables 1 and 2 and Figures 1 and 2.

3. Discussion

The solubilities of urea and hydrogen peroxide in water at 273.15 K and 283.15 K were examined in this paper. The results show the formation of two solid phases, $CO(NH_2)_2 \cdot H_2O_2$ and $CO(NH_2)_2$. In Figures 1 and 2, within the region CM, linking the component points of the liquid phase and the moist solid phase and extended, the point of intersection of these tie lines is approximately the solid-phase component for the compound ($CO(NH_2)_2 \cdot H_2O_2$) in the wet basis. The region PCM is the crystalline region of the pure compound $CO(NH_2)_2 \cdot H_2O_2$, and C is a cosaturated point of $CO(NH_2)_2$ and $CO(NH_2)_2 \cdot H_2O_2$. The region PCB is the crystalline region of the mixture of $CO(NH_2)_2$ and $CO(NH_2)_2 \cdot H_2O_2$, and the region BCD is the crystalline region of pure $CO(NH_2)_2$ where D is the percentage concentration of saturated solution at a certain temperature.

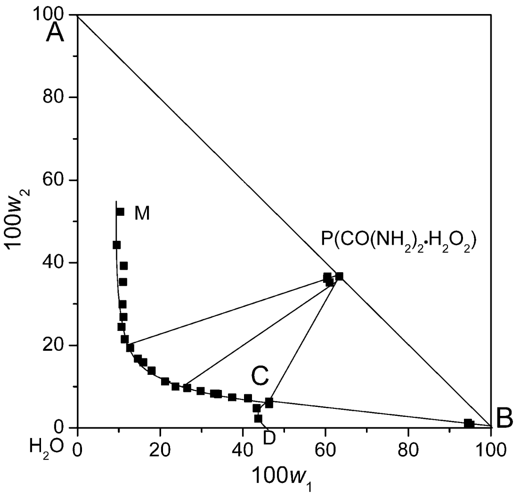

Figure 2. System urea + hydrogen peroxide + water at 283.15 K.

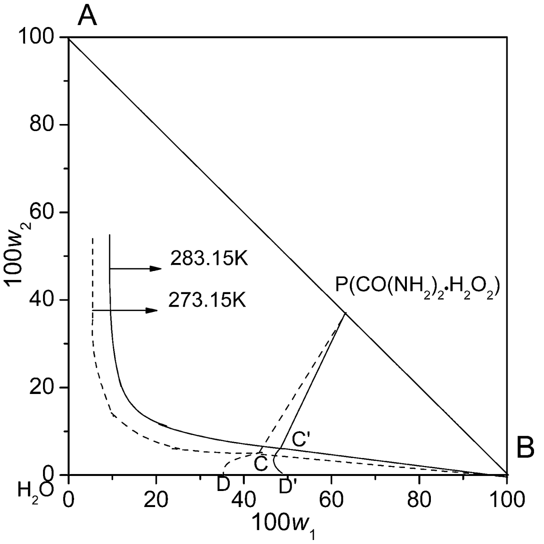

Figure 3. Multitemperature phase diagram at 273.15 K and 283.15 K.

The multitemperature phase of the system urea + hydrogen peroxide + water is shown in Figure 3, in which C and C′ are the cosaturated points of urea and the urea hydrogen peroxide adduct, respectively. The results indicated that the two solubility curves are similar at different temperatures. The crystalline region of the compound $CO(NH_2)_2 \cdot H_2O_2$ increases as the temperature decreases. The lower the temperature, the higher the yield of the compound $CO(NH_2)_2 \cdot H_2O_2$ and the availability of hydrogen peroxide.

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