Solid−Liquid Equilibrium for the Quaternary System of Sodium Carbonate + Sodium Chloride + Hydrogen Peroxide + Water at 293.15 K

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In this investigation, solid−liquid equilibrium for the quaternary system sodium carbonate + sodium chloride + hydrogen peroxide + water was studied at a temperature of 293.15 K using the moist solid method. Four solid phases were formed in the quaternary system that correspond to $Na_2CO_3 \cdot 10H_2O$, NaCl, $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$, and $Na_2CO_3 \cdot 2H_2O_2 \cdot H_2O$. The solubility fields of four solid phases were observed from the phase diagram. Results indicate that the crystallization field of $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$ is very large, the solubility of sodium percarbonate decreases with the increasing of sodium chloride content, and the product of sodium percarbonate can reach a high level. The solubility data and the quaternary phase diagram can provide the fundamental basis for the preparation of sodium percarbonate and optimize the preparing "wet process" and especially can serve as a guide for the preparation of sodium percarbonate with sodium chloride as the salting-out agent.

Introduction

Sodium carbonate forms a crystalline addition compound with hydrogen peroxide, corresponding to the formula $Na_2CO_3 \cdot 1.5H_2O_2$(sodium carbonate perhydrate), and is commonly known as sodium percarbonate. Although it has a wide range of uses employing its oxidant[1−4] and disinfectant[5−7] qualities, currently its most widespread use is as a bleach in washing compositions,[8−14] especially the compact and super-compact compositions that have been promoted by the detergent industry since the 1980s; or in dishwashing compositions;[15−17] or as a bleach additive.[18−20] As compared with a so-called chlorine bleaching agent, sodium percarbonate is slightly inferior in its bleaching effect. However, sodium percarbonate acts more gently, for example, on cloth, thereby not causing damage to the fibers. Furthermore, sodium percarbonate does not produce a poisonous gas such as chlorine. In the move to formulate "greener" products, the use of sodium percarbonate to replace chlorine as a bleaching agent in or with detergent composition is becoming increasingly prevalent, especially in zeolite-containing detergent compositions. Thus, the compound has many potential applications as a peroxygen source when dissolved in an aqueous medium.

Sodium percarbonate can be produced by a variety of process routes, normally employing a reaction between hydrogen peroxide and a source of sodium carbonate. In some variations, often called collectively "wet processes", the sodium percarbonate crystallizes out of solution. During some reactions, sodium chloride is added as the salting-out agent in order to decrease the composition of sodium carbonate present in the mother solution as a further consequence enables greater production to be obtained from a reactor of a given size.[21−29] The use of a salting-out agent is a common practice in wet processes, in view of the significant advantages. It is well-known that the production of sodium percarbonate is based on the phase diagram of the quaternary system Na_2CO_3 + NaCl + H_2O_2 + H_2O. Although the ternary diagrams of the subsystems Na_2CO_3 + NaCl + H_2O,[28] Na_2CO_3 + H_2O_2 + H_2O,[28−31] and NaCl + H_2O_2 + H_2O[32] have been investigated, no studies have been reported on the phase diagram of the quaternary system. It is important to investigate the phase diagram for designing and optimizing the procedure of sodium percarbonate. The objective of this research is to investigate and generate the phase diagrams of quaternary system at 293.15 K by the moist solid method.

Experimental Section

Materials. The hydrogen peroxide used (not containing stabilizers) was produced by Jiangsu Yangnong Chemical Group Co. LTD, with a mass fraction of 75 %. The other chemicals, sodium carbonate (purity of 99.98 %) and sodium chloride (purity of 99.97 %), were of reagent quality. The water used to prepare solutions was twice distilled water (conductivity < 5 μS/cm).

Procedure. All measurement was made at 293.15 K. A known mass of sodium carbonate and sodium chloride was added into a conical flask with different mass fraction from 0 to 75 % of hydrogen peroxide. Fifteen flasks containing the same mixture with the same proportion of composition were placed in a bath controlled at a constant temperature. A 5.0 mL sample of the clarified solution was taken from the liquid phase of each conical flask with a pipet at regular intervals and diluted to 50 mL of solution in a volumetric flask filled with twice distilled water. If the results of chemical analysis in the bottle become constant, it indicated that equilibrium was achieved. Generally, it took about 6 h to reach equilibrium. After the equilibrium was accomplished, the solid and the liquid were separated by filtration and analyzed. This procedure was repeated with the ratio of sodium carbonate and sodium chloride varied.

Analysis. The sodium carbonate was determined by titrating with standard hydrochloric acid. The hydrogen peroxide concentration was determined by titrating the acidified solution with standard potassium permanganate. The sodium chloride concentration was determined by titrating with a standard solution

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Table 1. Mass Fraction Solubilities of the Quaternary System Sodium Carbonate (1) + Sodium Chloride (2) + Hydrogen Peroxide (3) + Water (4) at 293 K[a]

mass fraction								Jãneck neck index/[kg/100 kg of dry salt]								
liquid phase				moist solid phase				liquid phase				solid phase				solid phase
100 w_1	100 w_2	100 w_3	100 w_4	100 w_1	100 w_2	100 w_3	100 w_4	H_2O_2	NaCl	Na_2C0_3	H_2O	H_2O_2	NaCl	Na_2C0_3	H_2O	
								E_1P_1								
0.99	1.17	23.33	74.51	5.33	1.11	40.39	53.17	3.88	4.60	91.52	292.30	11.37	2.38	86.25	113.52	N_{10} + A
0.92	3.09	20.86	75.13	5.40	3.01	39.68	51.91	3.71	12.41	83.88	302.12	11.23	6.25	82.52	107.96	N_{10} + A
0.82	5.04	19.05	75.09	7.71	4.26	39.50	48.53	3.31	20.23	76.46	301.32	14.98	8.27	76.75	94.31	N_{10} + A
0.89	6.50	18.02	74.59	7.38	6.66	40.49	45.47	3.52	25.59	70.89	293.45	13.54	12.21	74.25	83.40	N_{10} + A
0.80	8.39	17.23	73.58	9.59	8.38	42.41	39.62	3.01	31.77	65.22	278.55	15.87	13.88	70.21	65.57	N_{10} + A
0.59	10.78	16.76	71.87	9.65	12.00	42.49	35.86	2.09	38.32	59.59	255.62	15.04	18.71	66.25	55.91	N_{10} + A
0.60	13.13	16.33	69.94	7.86	16.89	41.72	33.53	2.00	43.68	54.32	232.69	11.82	25.41	62.76	50.44	N_{10} + A
0.41	14.14	16.09	69.36	8.55	20.41	42.41	28.63	1.34	46.14	52.52	226.34	11.98	28.60	59.42	40.11	N_{10} + A
								E_2P_1								
0.25	17.87	16.04	65.84	8.80	23.15	43.68	24.37	0.74	52.31	46.95	192.76	11.64	30.61	57.75	32.20	N_{10} + A
								P_1P_2								
0.71	17.38	13.00	68.91	11.18	42.64	36.13	10.05	2.28	55.91	41.81	221.62	12.43	47.42	40.18	11.21	N + A
0.48	18.36	11.50	69.66	11.86	45.52	32.63	9.99	1.58	60.51	37.91	229.64	13.18	50.57	36.25	11.10	N + A
0.54	19.53	8.97	70.96	10.84	51.73	27.68	9.75	1.86	67.26	30.88	244.31	12.01	57.32	30.67	10.81	N + A
0.44	21.38	6.43	71.75	10.15	57.35	23.18	9.32	1.55	75.70	22.75	254.04	11.19	63.25	25.56	10.28	N + A
0.57	22.34	4.94	72.15	6.63	66.61	18.15	8.61	2.03	80.24	17.73	259.22	7.26	72.88	19.86	9.42	N + A
0.52	24.21	2.78	72.49	5.70	72.36	13.97	7.97	1.89	87.99	10.12	263.46	6.19	78.63	15.18	8.66	N + A
0.95	25.10	1.29	72.66	5.30	77.69	10.31	6.70	3.49	91.80	4.71	265.70	5.68	83.32	11.06	7.25	N + A
3.58	23.55	0.69	72.18	9.22	51.76	16.72	22.30	12.88	84.63	2.49	259.41	11.87	66.63	21.53	28.73	N + A
6.98	22.17	0.76	70.09	14.64	38.29	26.13	20.94	23.34	74.13	2.53	234.32	18.51	48.42	33.04	26.45	N + A
10.08	21.35	0.78	67.79	12.71	44.35	24.01	18.93	31.31	66.28	2.41	210.50	5.68	54.70	29.62	23.34	N + A
13.20	20.37	1.22	65.21	17.00	31.16	30.22	21.62	37.93	58.55	3.52	187.42	21.69	39.76	38.55	27.58	N + A
15.05	20.26	1.17	63.52	15.94	35.61	28.69	19.76	41.25	55.53	3.22	174.13	19.86	44.38	35.76	24.63	N + A
20.38	20.15	1.41	58.06	18.64	28.28	34.11	18.97	48.60	48.05	3.35	138.42	23.00	34.90	42.10	23.42	N + A
28.59	20.98	1.60	48.83	21.14	24.75	37.86	16.25	55.88	41.00	3.12	95.42	25.24	29.55	45.21	19.41	N + A
								E_3P_2								
33.13	10.89	4.65	51.33	31.89	0.67	56.41	11.03	68.06	22.38	9.56	105.42	35.85	0.75	63.42	12.42	A + B
31.15	3.55	6.39	58.91	32.66	1.39	54.32	11.63	75.81	8.64	15.55	143.40	36.96	1.57	61.47	3.17	A + B
								P_2T								
38.55	25.08	1.18	35.19	27.41	31.53	32.74	8.32	59.48	38.70	1.82	54.30	29.90	34.39	35.71	9.07	B + N

[a] N_{10}, $Na_2CO_3 \cdot 10H_2O$; A, $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$; N, NaCl; B, $Na_2CO_3 \cdot 2H_2O_2 \cdot H_2O$; w, mass fraction.

of silver nitrate in the presence of three drops of potassium chromate solution with mass fraction 0.1 % as an indicator. Each analysis was repeated three times, and the average value of three measurements was considered as the final value of the analysis (precision: 0.1 %). The accuracy of the thermostat temperature was 0.1 K. In these studies, X-ray diffraction and infrared absorption spectroscopy were also employed to determine whether the solid phase was pure or compound.

Results and Discussion

The solubility data of the quaternary system Na_2CO_3 + NaCl + H_2O_2 + H_2O 293.15 K are shown in Table 1. There are four solid phases formed in solution that correspond to $Na_2CO_3 \cdot 10H_2O$, NaCl, $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$, and $Na_2CO_3 \cdot 2H_2O_2 \cdot H_2O$, respectively. It should be noted that the solubility data of the ternary system Na_2CO_3 + NaCl + H_2O and Na_2CO_3 + H_2O_2 + H_2O at 293.15 K are taken from the literature,[28] and those of the system NaCl + H_2O_2 + H_2O are taken from the literature.[29]

Figure 1 is the three-dimensional diagram of the quaternary system. Figure 2 is the projection of phase diagram.

NN′HH′ is the phase diagram of the ternary system Na_2CO_3 + H_2O_2 + H_2O 293.15 K in Figure 1. Curve $N_{10}E_1$ corresponds to the crystallization line of the salt $Na_2CO_3 \cdot 10H_2O$; curve E_1ME_3 corresponds to the crystallization line of the salt $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$; curve E_3C corresponds to the crystallization line of the salt $Na_2CO_3 \cdot 2H_2O_2 \cdot H_2O$. E_1 and E_3 are cosaturated points with $Na_2CO_3 \cdot 10H_2O$, $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$, $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$, and $Na_2CO_3 \cdot 2H_2O_2 \cdot H_2O$.

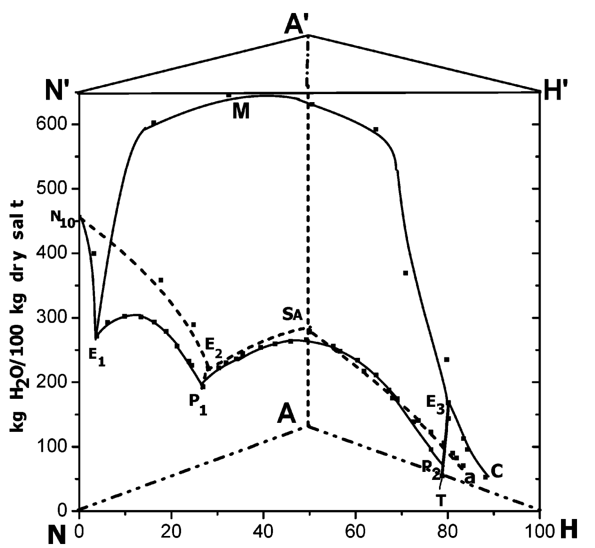

Figure 1. Three-dimensional phase diagram of the quaternary system Na_2CO_3 + NaCl + H_2O_2 + H_2O 293.15 K. A, NaCl; N, Na_2CO_3; H, H_2O_2; N_{10}, solubility of Na_2CO_3 in H_2O at 293.15 K; S_A, solubility of NaCl in H_2O at 293.15 K. The other symbols have the same meaning as those described in Table 1. E_1, cosaturated point of a solution with solid phases $Na_2CO_3 \cdot 10H_2O$ and $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$; E_2, cosaturated point of a solution with solid phases $Na_2CO_3 \cdot 10H_2O$ and NaCl; E_3, cosaturated point of a solution with solid phases $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$ and $Na_2CO_3 \cdot 2H_2O_2 \cdot H_2O$; P_1, cosaturated point of a solution with solid phases $Na_2CO_3 \cdot 10H_2O$, $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$, and NaCl; P_2, cosaturated point of a solution with solid phases NaCl, $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$, and $Na_2CO_3 \cdot 2H_2O_2 \cdot H_2O$.

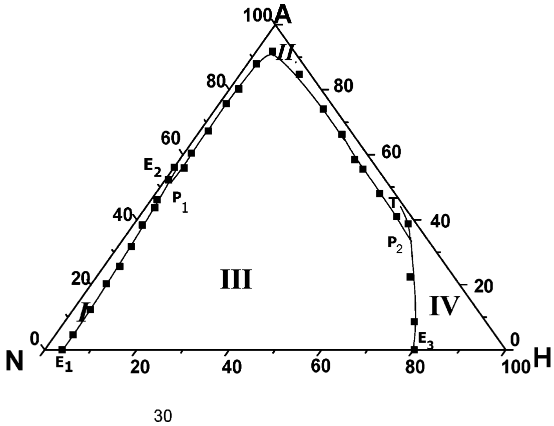

Figure 2. Dry salt phase diagram of the quaternary system Na_2CO_3 + NaCl + H_2O_2 + H_2O at 293.15 K. The other symbols have the same meaning as those described in Figure 1.

NN′AA′ is the diagram of the ternary system Na_2CO_3 + NaCl + H_2O 293.15 K in Figure 1. Curve $N_{10}E_2$ corresponds to the crystallization line of the salt $Na_2CO_3 \cdot 10H_2O$; curve E_2S_A corresponds to the crystallization line of the salt NaCl; E_2 is cosaturated points with $Na_2CO_3 \cdot 10H_2O$ and NaCl.

HH′AA′ is the diagram of the ternary system NaCl + H_2O_2 + H_2O 293.15 K in Figure 1. Curve S_A corresponds to the crystallization line of the salt NaCl.

Figure 2 show that the diagram is divided into four crystallization fields by five curves: curve E_1P_1, corresponding to the crystallization line of the salt $Na_2CO_3 \cdot 10H_2O$ and $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$ with the saturated solution; curve E_2P_1, corresponding to the crystallization line of the salt $Na_2CO_3 \cdot 10H_2O$ and NaCl with the saturated solution; curve P_1P_2, corresponding to the crystallization line of the salt NaCl and $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$ with the saturated solution; curve P_2T, corresponding to the crystallization line of the salt $Na_2CO_3 \cdot 2H_2O_2 \cdot H_2O$ and NaCl; curve P_2E_3, corresponding to the crystallization line of the salt $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$ and $Na_2CO_3 \cdot 2H_2O_2 \cdot H_2O$. There are four crystalline zones of pure solids: I, corresponding to the equilibrium of the salt $Na_2CO_3 \cdot 10H_2O$ with the saturated solution; II, corresponding to the equilibrium of the salt NaCl with the saturated solution; III, corresponding to the equilibrium of the salt $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$ with the saturated solution; IV, corresponding to the equilibrium of the salt $Na_2CO_3 \cdot 2H_2O_2 \cdot H_2O$ with the saturated solution.

There are two isothermal invariant points P_1 and P_2. Point P_1 is represented by the solution composition being in equilibrium with salts $Na_2CO_3 \cdot 10H_2O$, NaCl, and $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$. Whereas point P_2 represents the solution composition being in equilibrium with the salts NaCl, $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$, and $Na_2CO_3 \cdot 2H_2O_2 \cdot H_2O$.

In Figure 1, $N_{10}E_1P_1E_2$ represents the crystallization field of the salt $Na_2CO_3 \cdot 10H_2O$; $P_2P_1E_2S_A$ represents the crystallization field of the salt NaCl; $E_3E_1P_1P_2$ represents the crystallization field of the salt $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$; CE_3P_2T is the crystallization field of the salt $Na_2CO_3 \cdot 2H_2O_2 \cdot H_2O$.

Conclusion

The solubility data of the quaternary system Na_2CO_3 + NaCl + H_2O_2 + H_2O at 293.15 K are measured by using moist solid method; the phase diagram is constructed. There are four solid phases formed in the quaternary system that correspond to $Na_2CO_3 \cdot 10H_2O$, NaCl, $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$, and $Na_2CO_3 \cdot 2H_2O_2 \cdot H_2O$. This work can serve as a guide for the preparation of sodium percarbonate with sodium chloride as the salting-out agent.

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