Articles

Phase Diagram for the System KOH + K_2CrO_4 + KCl + H_2O

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The solubilities of the K_2CrO_4 + KCl + KOH + H_2O system at 20 °C, 40 °C, 60 °C, and 80 °C were determined by an isothermal method, and the phase diagrams were constructed. Meanwhile, the concentration of K_2CrO_4 in an aqueous solution of KOH was compared with that in an aqueous solution of KOH saturated with KCl. Lastly, analyses and discussions were made on the crystalline areas in the phase diagrams.

Introduction

Chromium compounds play a very important role in many industrial processes and are widely applied in the manufacture of pigment, wood preservation, leather tanning, metal plating, and so on. The high-temperature roasting technology presently used in China discharges a large amount of chromium-containing residue, chromite dust, and waste gas, which severely pollute the environment. A new clean production technology of chromate has been proposed by the Institute of Process Engineering, Chinese Academy of Sciences, to replace the traditional production technology of chromate. In this new technology the reaction temperature can be significantly reduced, and higher resource utilization efficiency and zero emission of waste residue can be achieved.[1,2] The whole conversion process is based on the liquid-phase oxidation process of chromite with the molten KOH as the reaction medium. After the liquid-phase oxidation process of chromite and the separation process of chromate and alkali, excessive potassium hydroxide solution will go back to the process of the liquid-phase oxidation. However, with the reuse of KOH and enlargement of production, KCl can accumulate to a certain amount in the KOH as an impurity and influence the quality of potassium chromate. Thus, the phase equilibrium for the quaternary system K_2CrO_4 + KCl + KOH + H_2O is required to get high-quality potassium chromate.

Some studies[3−5] have been done on the solubility of relevant systems, such as the quaternary system KOH + K_2CrO_4 + K_2CO_3 + H_2O, K_2CrO_4 + KCl + H_2O, and K_2CrO_4 + K_2CO_3 + H_2O, but a study of the quaternary system KOH + K_2CrO_4 + KCl + H_2O has not been reported so far.

In this paper, the phase equilibrium for the latter system is studied in detail.

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Experimental Section

Apparatus and Reagents. A HZQ-C-type thermostatted water bath (CH-2501) with a precision of 0.1 °C and a specially designed rotating stainless steel disk were used for the equilibrium measurements.[6] A Siemens D500 X-ray diffraction analyzer was used for solid-phase X-ray diffraction analysis.

The main chemicals used were all of analytical grade and purchased from the Beijing Chemical Plant: potassium chromate (≥ 99.5 % by mass), potassium hydroxide (≥ 99.0 % by mass), and potassium chloride (≥ 99.8 % by mass).

Experimental Method. The solubility was determined by employing the method of isothermal solution saturation. The experiments were performed according to the following procedure: The experimental components were added into a series of sealed tubes gradually according to a fixed ratio and making sure that two of the components were in excess. The disk with the sealed tubes was then put into the superthermostatic water bath and rotated continuously at the four specific temperatures: 20 °C, 40 °C, 60 °C, and 80 °C. A pre-experiment showed that equilibrium can be reached in about 3 to 4 days. In order to guarantee the system reaching the total equilibrium, the stirring lasted 5 days. After equilibrium, the agitating was stopped and the system then was allowed to stand for at least 24 h to ensure all the suspended crystals settled. Then 5 mL of the liquid phases was taken from every tube and analyzed. The solid phases were dried, pestled into powder, and analyzed by X-ray diffraction.

Analytical Method. The hydroxyl ion OH^- was determined by hydrochloric acid solution using phenolphthalein solution as indicator (with a mass uncertainty of 0.6 %), the chromate ion CrO_4^{2-} was titrated using *N*-phenylanthranilic acid solution as indicator (with a mass uncertainty of 1.5 %), the amount of chloride was found argentometrically by the Mohr method (with a mass uncertainty of 0.3 %), and the potassium ion was analyzed by a gravimetric method with sodium tetraphenylboron (with a mass uncertainty of 0.5 %). Each experimental result was achieved from the mean values of three parallel determinations.

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Table 1. Solubility Data of the KOH (1) + K_2CrO_4 (2) + KCl (3) + H_2O (4) System

composition of the liquid phase (g/100 g of dry salt)					
KOH	K_2CrO_4	KCl	H_2O	ρ/(kg·dm^{-3})	Equilibrium solid phases
T = 20 °C					
7.52	47.04	45.44	225.44	1.307	K_2CrO_4 + KCl
33.82	26.81	39.37	241.19	1.296	K_2CrO_4 + KCl
46.65	22.99	30.35	212.88	1.297	K_2CrO_4 + KCl
54.55	17.72	27.73	210.93	1.281	K_2CrO_4 + KCl
61.59	13.81	24.60	209.10	1.294	K_2CrO_4 + KCl
70.42	9.30	20.28	203.39	1.295	K_2CrO_4 + KCl
72.40	8.49	19.12	203.74	1.296	K_2CrO_4 + KCl
75.58	6.98	17.44	199.98	1.309	K_2CrO_4 + KCl
77.98	6.03	15.99	195.79	1.311	K_2CrO_4 + KCl
86.08	3.11	10.81	180.07	1.337	K_2CrO_4 + KCl
89.87	1.85	8.28	173.28	1.356	K_2CrO_4 + KCl
91.02	1.63	7.35	170.44	1.356	K_2CrO_4 + KCl
93.11	1.37	5.52	152.38	1.385	K_2CrO_4 + KCl
93.33	1.32	5.35	150.68	1.379	K_2CrO_4 + KCl
95.32	0.42	4.26	141.41	1.426	K_2CrO_4 + KCl
97.07	0.34	2.58	117.79	1.479	K_2CrO_4 + KCl
98.02	0.11	1.88	103.42	1.515	K_2CrO_4 + KCl + KOH·$2H_2O$
0	53.64	46.36	216.84	1.325	K_2CrO_4 + KCl
98.34	0	1.66	99.89	1.515	KCl + KOH·$2H_2O$
99.98	0.02	0	101.51	1.528	K_2CrO_4 + KOH·$2H_2O$
T = 40 °C					
13.96	41.43	44.61	153.66	1.294	K_2CrO_4 + KCl
20.33	32.07	47.60	199.94	1.298	K_2CrO_4 + KCl
28.38	27.41	44.21	207.80	1.295	K_2CrO_4 + KCl
36.59	24.98	38.44	197.92	1.297	K_2CrO_4 + KCl
49.19	18.04	32.77	183.94	1.288	K_2CrO_4 + KCl
55.07	14.88	30.05	185.94	1.293	K_2CrO_4 + KCl
63.16	11.12	25.71	182.70	1.293	K_2CrO_4 + KCl
73.63	6.96	19.41	182.26	1.347	K_2CrO_4 + KCl
79.02	4.87	16.11	173.91	1.349	K_2CrO_4 + KCl
81.30	4.17	14.53	164.39	1.321	K_2CrO_4 + KCl
87.85	2.18	9.96	143.14	1.316	K_2CrO_4 + KCl
89.38	1.77	8.85	155.75	1.379	K_2CrO_4 + KCl
92.34	1.11	6.55	143.07	1.396	K_2CrO_4 + KCl
94.73	0.94	4.33	142.46	1.406	K_2CrO_4 + KCl
95.01	0.83	4.16	133.26	1.420	K_2CrO_4 + KCl
96.94	0.43	2.63	114.38	1.463	K_2CrO_4 + KCl
97.69	0.28	2.03	105.31	1.488	K_2CrO_4 + KCl l
98.42	0.15	1.43	89.02	1.537	K_2CrO_4 + KCl + KOH·$2H_2O$
0	56.09	43.91	120.77	1.327	K_2CrO_4 + KCl
98.56	0	1.44	82.96	1.534	KCl + KOH·$2H_2O$
99.87	0.125	0	87.01	1.541	K_2CrO_4 + KOH·$2H_2O$
T = 60 °C					
3.32	48.04	48.64	146.31	1.273	K_2CrO_4 + KCl
10.37	44.96	44.68	157.66	1.276	K_2CrO_4 + KCl
26.13	32.22	41.66	171.36	1.294	K_2CrO_4 + KCl
35.92	24.48	39.60	173.72	1.303	K_2CrO_4 + KCl
44.86	20.26	34.88	176.26	1.300	K_2CrO_4 + KCl
48.56	17.95	33.50	172.55	1.309	K_2CrO_4 + KCl
59.22	12.56	28.22	172.89	1.312	K_2CrO_4 + KCl
63.96	10.42	25.62	180.91	1.323	K_2CrO_4 + KCl
66.88	9.34	23.77	174.06	1.331	K_2CrO_4 + KCl
75.34	5.99	18.67	164.53	1.342	K_2CrO_4 + KCl
80.33	3.79	15.88	157.90	1.363	K_2CrO_4 + KCl
82.24	3.28	14.48	159.29	1.367	K_2CrO_4 + KCl
86.07	2.35	11.57	148.20	1.382	K_2CrO_4 + KCl
89.67	1.80	8.54	126.24	1.402	K_2CrO_4 + KCl
96.80	0.27	2.93	100.54	1.510	K_2CrO_4 + KCl + KOH·$2H_2O$
0	50.39	49.61	148.60	1.330	K_2CrO_4 + KCl
97.78	0	2.22	73.36	1.559	KCl + KOH·$2H_2O$
99.84	0.16	0	87.92	1.545	K_2CrO_4 + KOH·$2H_2O$
T = 80 °C					
3.33	47.68	48.98	129.24	1.328	K_2CrO_4 + KCl
8.95	42.78	48.26	138.00	1.315	K_2CrO_4 + KCl
15.41	37.49	47.10	149.93	1.311	K_2CrO_4 + KCl
22.94	32.50	44.56	158.79	1.313	K_2CrO_4 + KCl
32.90	27.07	40.03	145.20	1.317	K_2CrO_4 + KCl
37.18	24.28	38.55	150.28	1.316	K_2CrO_4 + KCl
47.31	18.76	33.93	154.71	1.325	K_2CrO_4 + KCl
52.53	16.01	31.46	155.95	1.326	K_2CrO_4 + KCl
59.22	11.59	29.20	162.08	1.328	K_2CrO_4 + KCl
65.05	9.47	25.48	159.70	1.335	K_2CrO_4 + KCl
69.38	7.41	23.20	159.78	1.337	K_2CrO_4 + KCl
73.35	6.14	20.51	163.80	1.340	K_2CrO_4 + KCl
76.91	4.89	18.20	148.48	1.355	K_2CrO_4 + KCl
80.60	3.77	15.63	144.91	1.368	K_2CrO_4 + KCl
82.28	3.14	14.58	144.18	1.352	K_2CrO_4 + KCl
85.65	2.36	11.99	120.95	1.328	K_2CrO_4 + KCl
90.71	1.59	7.70	119.64	1.433	K_2CrO_4 + KCl
95.26	0.55	4.19	91.45	1.520	K_2CrO_4 + KCl
96.87	0.24	2.89	75.42	1.555	K_2CrO_4 + KOH·$2H_2O$
0	49.90	50.10	145.13	1.361	K_2CrO_4 + KCl
97.03	0	2.97	72.41	1.528	KCl + KOH·$2H_2O$
99.77	0.23	0	76.43	1.569	K_2CrO_4 + KOH·$2H_2O$

Results and Discussion

The solubilities of the K_2CrO_4 + KCl + KOH + H_2O system at 20 °C, 40 °C, 60 °C, and 80 °C were determined and are presented in Table 1. The phase diagrams from 20 °C and 80 °C are plotted in Figures 1 and 2. The phase diagrams for the other two temperatures are similar.

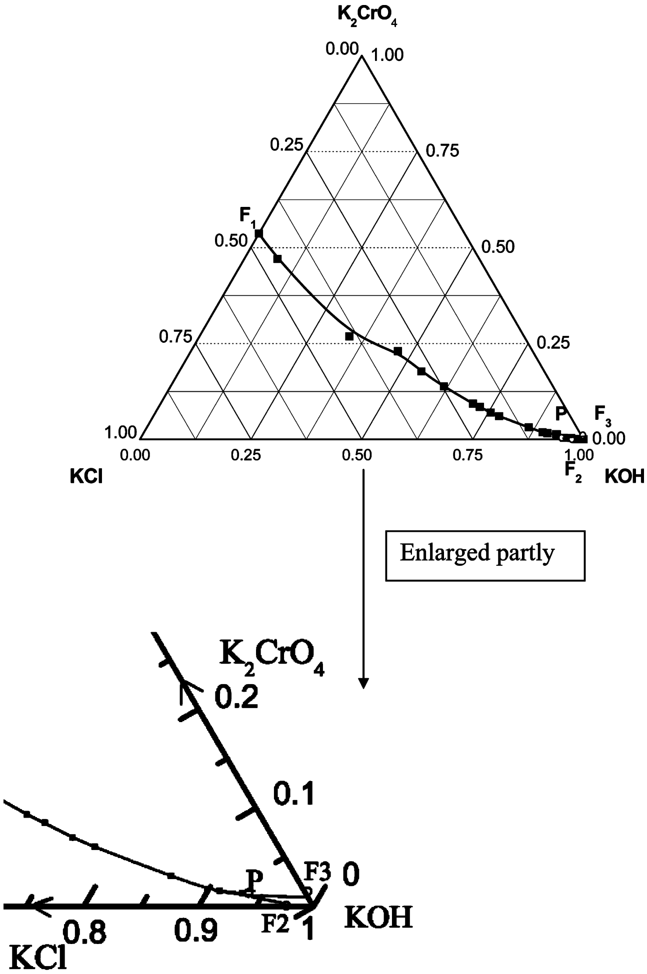

Figure 1. Phase diagram of the KOH (1) + K_2CrO_4 (2) + KCl (3) + H_2O (4) system at 20 °C.

Figures 1 and 2 show that the system has three crystallization zones: the K_2CrO_4 crystallization zone, the KCl crystallization zone, and the $KOH \cdot 2H_2O$ crystallization zone.

Points F1, F2, and F3 represent the equilibrium of the solid phases at the two extremes of the corresponding side. Point P is an invariant point, which represents the equilibrium of all three solid phases.

As can be seen in Figures 1 and 2, the solubility of K_2CrO_4 and KCl decreases greatly with an increase in the KOH concentration, and the crystallization zones of K_2CrO_4 and KCl are far larger than that of $KOH \cdot 2H_2O$, so K_2CrO_4 and KCl crystals will precipitate together while the amount of water is suitable. As shown in Figure 3, the concentration of K_2CrO_4 declines sharply because of the existence of KCl in the system. This means that the salting out effect of KCl to K_2CrO_4 is strong and K_2CrO_4 crystals can be precipitated more easily. The results are similar at 20 °C, 40 °C, and 60 °C.

In Figure 4, the solubility of K_2CrO_4 decreases faster than KCl with an increase of the concentration of KOH. In addition, when the concentration of KOH reaches 500 $g \cdot L^{-1}$, the solubility of KCl in the solution overtakes that of K_2CrO_4 a lot. It also can be seen that the solubilities of both K_2CrO_4 and KCl decrease with a decrease of the temperature.

According to the analysis above, the whole separation process can be designed as follows. First, the coarse crystalline K_2CrO_4 carrying the impurity KCl was added into the high alkaline solution at 80 °C, where the concentration of KOH exceeds 500 $g \cdot L^{-1}$, and making sure that the KCl in the alkaline solution can just get saturated. Then most of the K_2CrO_4 crystals can be separated from the solution through high-temperature filtration

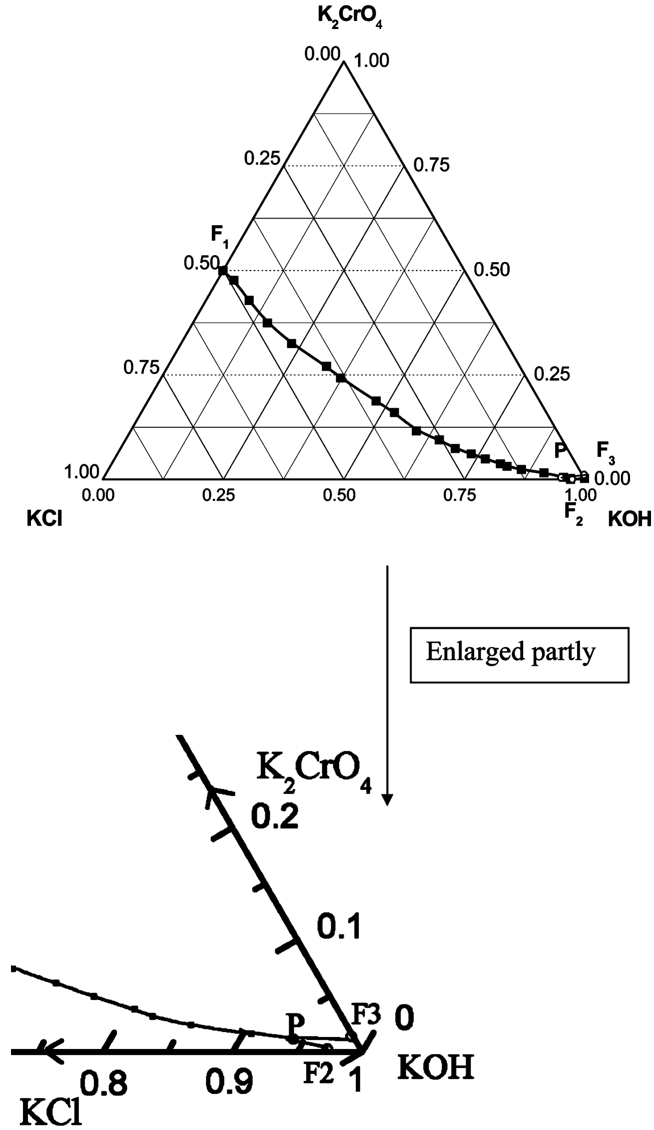

Figure 2. Phase diagram of the KOH (1) + K_2CrO_4 (2) + KCl (3) + H_2O (4) system at 80 °C.

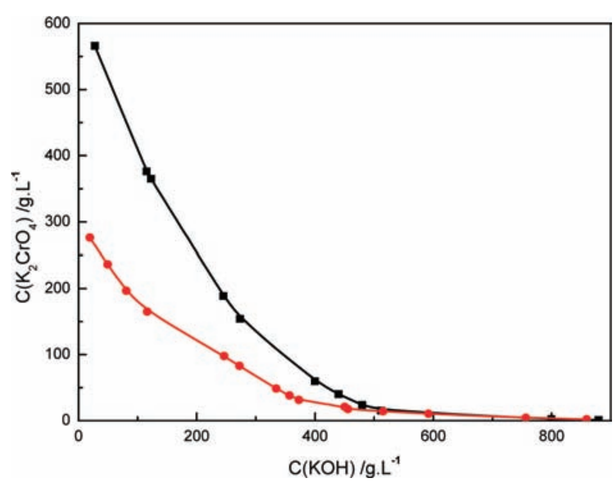

Figure 3. Solubility isotherms of K_2CrO_4 (2) at 80 °C: ■, in KOH (1) aqueous solution and ●, in KOH aqueous solution saturated with KCl (3).

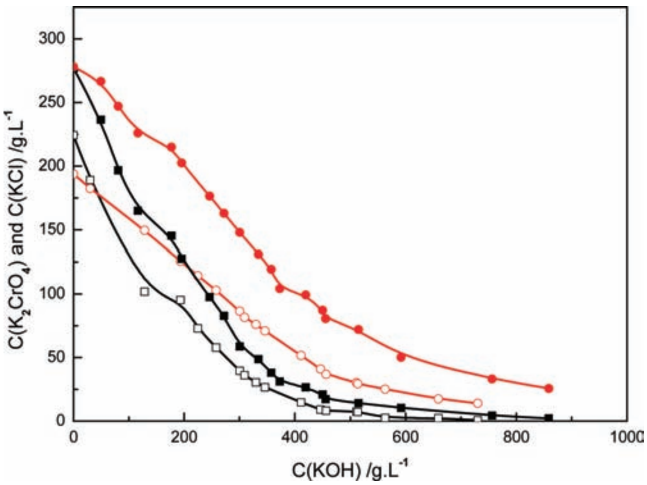

Figure 4. Solubility isotherms in KOH (1) aqueous solution: □, K_2CrO_4 (2) at 20 °C; ○, KCl (3) at 20 °C; ■, K_2CrO_4 (2) at 80 °C; and ●, KCl (3) at 80 °C.

at 80 °C. Second, making the alkaline solution cool off naturally from 80 °C to 20 °C, one-half of the KCl crystals with a small mount of K_2CrO_4 will be precipitated from the solution. Finally, the rest of the alkaline solution can be recycled to the first step after separation of the KCl crystals.

Conclusions

Phase equilibrium data for the system K_2CrO_4 + KCl + KOH + H_2O between 20 °C and 80 °C were studied. According to the solubility data measured, the phase diagrams were plotted, and analyses and discussions were made based on the phase diagram. The studies in the paper will have a positive role in the cleaner production of potassium chromate.

Literature Cited

(1) Zhang, Y.; Li, Z. H.; Qi, T.; Zheng, S. L.; Li, H. Q.; Xu, H. B. Green manufacturing process of chromium compounds. *Environ. Prog.* **2005**, *24* (1), 44–50.

(2) Zhang, Y.; Li, Z. H.; Qi, T.; Wang, Z. K. Green chemistry of chromate cleaner production. *Chin. J. Chem.* **1999**, *17*, 258–266.

(3) Cui, J. L.; Zhang, Y. Study on the KOH + K_2CrO_4 + K_2CO_3 + H_2O system. *J. Chem. Eng. Data* **2000**, *45*, 1215–1217.

(4) Christomir, C.; Jakubam, I.; Snejana, V.; Stefan, T. Thermodynamic study of aqueous sodium and potassium chloride and chromate systems at the temperature 298.15K. *J. Chem. Thermodyn.* **2002**, *34*, 987−994.

(5) Du, C. H.; Zheng, S. L.; Li, H. Q.; Zhang, Y. Solid-Liquid Equilibria of K_2CO_3 + K_2CrO_4 + H_2O System. *J. Chem. Eng. Data* **2006**, *51*, 1215–1217.

(6) Cao, D.; Zhang, Y.; Qi, T.; Chu, J.; Wang, L.; Zhang, Y. Phase diagram for the system $K_2Cr_2O_7$ + CrO_3 + H_2O at (25 and 90) °C. *J. Chem. Eng. Data* **2007**, *52*, 766–768.

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