Phase Diagram for the System $K_2Cr_2O_7 + CrO_3 + H_2O$ at (25 and 90) °C

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Phase equilibrium data for the system $K_2Cr_2O_7 + CrO_3 + H_2O$ at (25 and 90) °C were determined by an isothermal method. The corresponding phase diagrams were plotted, and the crystallization areas were analyzed and discussed. The results show that CrO_3, $K_2Cr_2O_7$, $K_2Cr_3O_{10}$, and $K_2Cr_4O_{13}$ are present as solid phases in the system. Results from the study can be used as a basis for the separation of $K_2Cr_2O_7$ and CrO_3 in the cleaner production of chromium trioxide by an electrosynthesis process.

Introduction

Chromium trioxide is an important chromium compound and accounts for the production of nearly 60 % of all chromium derivatives. In the industrial manufacture of chromium trioxide, the traditional method of decomposing sodium dichromate using sulfuric acid is widely applied. However, the long-flow process discharges large amounts of high chromium-containing waste solutions that can cause serious environmental problems. The resource utilization efficiency of the process is low, and it is difficult to recycle sodium or potassium within the system.

Therefore, a green process with zero emission of waste was sought, and to this end, the manufacturing of chromium trioxide by electrolyzing dichromate salts[1,2] has been studied. This process was carried out in an electrochemical cell that contains an ion-exchange membrane. The main reactions in the electrolysis of sodium dichromate are as follows:

In the anode cell:

$$H_2O - 2e^- = 2H^+ + 1/2O_2$$

In the cathode cell:

$$Na_2Cr_2O_7 + 2H^+ = H_2Cr_2O_7 + 2Na^+$$

$$2H_2O + 2e^- = 2OH^- + H_2$$

$$2Na^+ + 2OH^- = 2NaOH$$

The full reaction:

$$Na_2Cr_2O_7 + 3H_2O = H_2Cr_2O_7 + 2NaOH + H_2 + 1/2O_2{}^3$$

Then the solution in the anode cell is separated by crystallization to obtain the CrO_3 product, and at the same time NaOH can be obtained from the solution in the cathode cell.

The manufacturing of chromium trioxide by electrolyzing potassium dichromate is advanced with the same reaction principle as mentioned above except that the green manufacturing process has been developed using potassium chromate as the intermediate.[4] Phase equilibrium information for the $K_2Cr_2O_7 + CrO_3 + H_2O$ system is required when investigating the separation process of $K_2Cr_2O_7$ and CrO_3. Some studies have been carried out on the solubility of the system $K_2O + CrO_3 + H_2O$ at (10, 30, and 60) °C.[5] However, phase equilibrium data for the system $K_2Cr_2O_7 + CrO_3 + H_2O$ at (25 and 90) °C have not been reported so far but is required for the separation of CrO_3 from $K_2Cr_2O_7$ solutions. In this paper, the phase equilibrium for the system above is studied in detail.

Experimental Section

Apparatus and Reagents. The chemicals used were all of analytical grade and produced by either the Tianjin Chemical plant or Beijing Chemical plants: potassium dichromate (≥ 99.8 mass %) and chromium trioxide (≥ 99.0 mass %). Double deionized water (made using a Millipore instrument) was used to prepare the series of solutions.

A super-thermostatic water bath (CH-2501) with a precision of ± 0.1 °C and a rotating stainless steel disk were used for the equilibrium measurements. An X-ray diffraction analyzer (XPert PRO MPD, Panalytical Instrument) was used for the analysis of the solid phase. An ICP-OES (Optimal 5300DV, Perkin-Elmer Instruments) was applied to analyze K^+.

Experimental Method. The solubility was determined by employing the method of isothermal solution saturation. The experiments were carried out according to the following procedure: the system points were prepared by adding the second component gradually to a saturated solution of the first single-component while at the same time making sure that there was enough solid in the solution for analysis of the solid phase. The mixtures were put into a series of sealed tubes separately, which was fixed on a stainless steel disk. The disk with the sealed tubes was rotated continuously in the super-thermostatic water bath at the fixed temperature (25 or 90 °C) until the mixture reached equilibrium. Our pre-experiment showed that equilibrium can be reached in about 4 days. The system was kept rotating for 5 days to make sure that equilibrium had been reached, and then it was left static for 1 h to ensure all suspended crystals settled. Samples of the solution and solid phases were then taken out and analyzed. The sampling equipment was preheated to a temperature slightly higher than the experimental temperature to prevent the possibility of crystallization. The sampling process lasted about 2 s. The solid phases were dried, pestled into power, and analyzed by X-ray diffraction.

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Table 1. Solubility Data of the $K_2Cr_2O_7$ (1) + CrO_3 (2) + H_2O (3) System at (25 and 90) °C

composition of liquid phase (mass %)			
100 w_1	100 w_2	100 w_3	equilibrium solid phases
	T = 25 °C		
0.00	63.20[7]	36.80	CrO_3
0.52	62.40	37.08	CrO_3
1.00	61.88	37.12	CrO_3
1.33	61.42	37.25	$K_2Cr_4O_{13}$ + CrO_3
1.45	60.19	38.36	$K_2Cr_4O_{13}$
1.43	59.43	39.14	$K_2Cr_4O_{13}$
2.20	54.29	43.51	$K_2Cr_4O_{13}$
2.86	51.76	45.38	$K_2Cr_4O_{13}$
3.66	49.64	46.70	$K_2Cr_4O_{13}$
5.10	46.82	48.08	$K_2Cr_4O_{13}$
6.43	44.38	49.19	$K_2Cr_3O_{10}$ + $K_2Cr_4O_{13}$
6.53	42.74	50.73	$K_2Cr_3O_{10}$
6.80	41.75	51.45	$K_2Cr_3O_{10}$
7.48	40.17	52.35	$K_2Cr_3O_{10}$
8.06	39.17	52.77	$K_2Cr_2O_7$ + $K_2Cr_3O_{10}$
7.56	36.64	55.80	$K_2Cr_2O_7$
7.04	34.22	58.74	$K_2Cr_2O_7$
6.78	30.62	62.60	$K_2Cr_2O_7$
6.53	26.87	66.60	$K_2Cr_2O_7$
6.72	22.59	70.69	$K_2Cr_2O_7$
7.20	17.50	75.30	$K_2Cr_2O_7$
7.80	13.43	78.77	$K_2Cr_2O_7$
9.50	8.23	82.27	$K_2Cr_2O_7$
13.30	0.00[7]	86.70	$K_2Cr_2O_7$
	T = 90 °C		
0.00	69.26[7]	30.74	CrO_3
2.30	68.20	29.50	CrO_3
3.98	66.70	29.32	CrO_3
6.70	65.11	28.19	CrO_3
9.87	63.27	26.86	$K_2Cr_4O_{13}$ + CrO_3
10.42	59.77	29.81	$K_2Cr_4O_{13}$
11.94	56.51	31.55	$K_2Cr_4O_{13}$
17.10	49.70	33.20	$K_2Cr_4O_{13}$
21.80	45.30	32.90	$K_2Cr_4O_{13}$
25.68	41.64	32.68	$K_2Cr_4O_{13}$
30.20	39.31	31.27	$K_2Cr_4O_{13}$
33.14	37.70	29.16	$K_2Cr_3O_{10}$ + $K_2Cr_4O_{13}$
35.30	35.85	28.85	$K_2Cr_3O_{10}$
38.16	33.40	28.44	$K_2Cr_3O_{10}$
41.59	30.47	23.67	$K_2Cr_3O_{10}$
45.41	27.05	27.54	$K_2Cr_3O_{10}$
46.29	25.36	28.35	$K_2Cr_2O_7$ + $K_2Cr_3O_{10}$
43.18	23.33	33.49	$K_2Cr_2O_7$
42.00	20.47	37.53	$K_2Cr_2O_7$
41.19	17.74	41.07	$K_2Cr_2O_7$
41.20	14.99	43.81	$K_2Cr_2O_7$
42.00	11.26	46.74	$K_2Cr_2O_7$
43.01	7.12	49.87	$K_2Cr_2O_7$
44.60	1.83	53.57	$K_2Cr_2O_7$
45.21[7]	0.00	54.79	$K_2Cr_2O_7$

Analytical Method. The samples were dissolved into water qualitatively. The total K^+ in the solution was determined by ICP-OES (uncertainty of 0.5 mass %), and the total Cr^{6+} was titrated using *N*-phenylanthranilic acid as the indicator (uncertainty of 0.1 mass %). The mass of $K_2Cr_2O_7$ was determined from the total amount of K^+, and the molality of CrO_3 can be calculated by subtracting the K^+ molality, which stands for the Cr^{6+} in the $K_2Cr_2O_7$ from the total Cr^{6+} molality. X-ray diffraction (XRD) was performed on an XPert PRO MPD X-ray instrument using Cu Kα radiation ($\lambda = 1.540$ Å) with a scan speed of 2° min^{-1}(from 5° to 90°).

Results and Discussions

The equilibrium data for the $K_2Cr_2O_7$ + CrO_3 + H_2O system at (25 and 90) °C are presented in Table 1. The respective concentration values are expressed in mass fraction. The corresponding phase diagrams at (25 and 90) °C are plotted in Figures 1 and 2, respectively. Figure 3 shows representative XRD patterns of the solid phases.

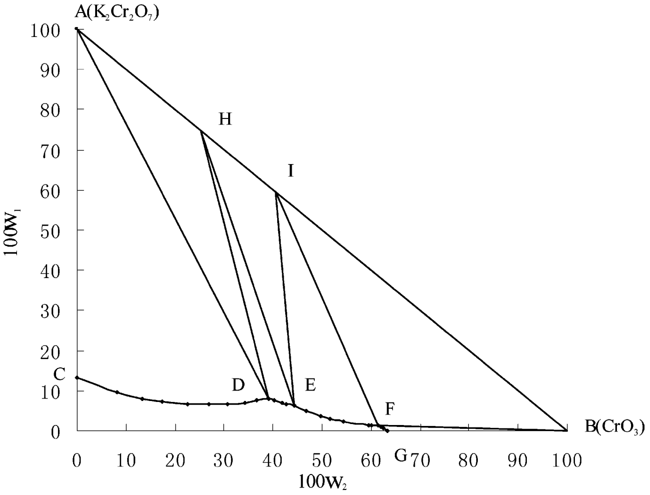

Figure 1. Phase diagram of the $K_2Cr_2O_7$ (1) + CrO_3 (2) + H_2O (3) system at 25 °C Experimental data points: A, solid-phase point ($K_2Cr_2O_7$); B, solid-phase point (CrO_3); C, binary system saturation point ($K_2Cr_2O_7-H_2O$); D, isothermally invariant point ($K_2Cr_2O_7-K_2Cr_3O_{10}$); E, isothermally invariant point ($K_2Cr_3O_{10}-K_2Cr_4O_{13}$); F, isothermally invariant point ($K_2Cr_4O_{13}-CrO_3$); G, binary system saturation point (CrO_3-H_2O); H, solid-phase point ($K_2Cr_3O_{10}$); I, solid-phase point ($K_2Cr_4O_{13}$).

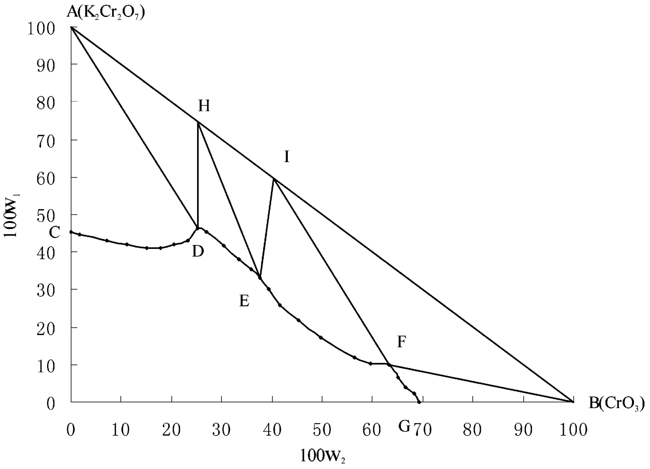

Figure 2. Phase diagram of the $K_2Cr_2O_7$ (1) + CrO_3 (2) + H_2O (3) system at 90 °C Experimental data points: A, solid-phase point ($K_2Cr_2O_7$); B, solid-phase point (CrO_3); C, binary system saturation point ($K_2Cr_2O_7-H_2O$); D, isothermally invariant point ($K_2Cr_2O_7-K_2Cr_3O_{10}$); E, isothermally invariant point ($K_2Cr_3O_{10}-K_2Cr_4O_{13}$); F, isothermally invariant point ($K_2Cr_4O_{13}-CrO_3$); G, binary system saturation point (CrO_3-H_2O); H, solid-phase point ($K_2Cr_3O_{10}$); I, solid-phase point ($K_2Cr_4O_{13}$).

As can be seen, the phase diagram at 25 °C is similar to the one at 90 °C. They both have four single crystallization zones according to the chemical analysis: the $K_2Cr_2O_7$ crystallization zone (ACD), the $K_2Cr_3O_{10}$ crystallization zone (DEH), the $K_2Cr_4O_{13}$[5, 6] crystallization zone (IEF), and the CrO_3 crystallization zone (BFG). The system has three isothermally invariant points (D, E, F) and four univariant curves (CD, DE, EF, FG). Points C and G show the solubilities of $K_2Cr_2O_7$ and CrO_3, respectively. The XRD data also show there are four solid phases presented in the system. The XRD patterns of $K_2Cr_2O_7$, $K_2Cr_3O_{10}$, and CrO_3 agree well with those of the X'Pert HighScore database. The XRD pattern of $K_2Cr_4O_{13}$ is not found in the reference. But the pattern of the sample we got in the experiment matches that of the standard $K_2Cr_4O_{13}$ purchased very well. The XRD results further proved the solid phases.

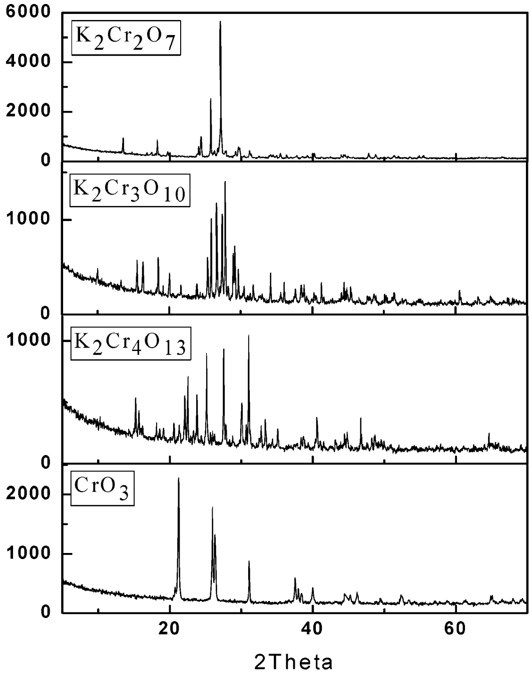

Figure 3. X-ray diffraction patterns of the solid phases.

Figures 1 and 2 show that temperature has a much stronger impact on the solubility of $K_2Cr_2O_7$ than that of CrO_3. The solubility of $K_2Cr_2O_7$ increases from 13.30 % at 25 °C to 45.21 % at 90 °C, while the solubility of CrO_3 increases less than 7 %. It also can be seen that the $K_2Cr_2O_7$ crystallization zone shrinks gradually and that the other three crystallization zones, especially the CrO_3 crystallization zone, expand with the increase of temperature. According to the phase diagram, in the separation process of $K_2Cr_2O_7$ and CrO_3, evaporating−cooling crystallization can be used to initially separate most of the $K_2Cr_2O_7$ in the solution, and then CrO_3 could be attained by evaporating the rest solution by controlling the operational conditions.

Conclusions

Phase equilibrium data for the system $K_2Cr_2O_7 + CrO_3 + H_2O$ at (25 and 90) °C were studied, and the phase diagrams were plotted. The XRD analysis indicated that there are four solid phases. The $K_2Cr_2O_7$ crystallization zone shrinks and the CrO_3 crystallization zone expands with the increase in temperature. The study can be used as a basis for the separation of CrO_3 from $K_2Cr_2O_7$ solutions, giving a cleaner production technology for chromium trioxide using an electrosynthetic process.

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