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Solubility in the $K_2Cr_2O_7 + CrO_3 + KNO_3 + HNO_3 + H_2O$ System

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The solubilities of the $K_2Cr_2O_7 + CrO_3 + KNO_3 + HNO_3 + H_2O$ system at 0 °C, 25 °C, and 45 °C were determined, and the phase diagrams were constructed. Furthermore, analyses and discussions are made on the crystalline areas in the phase diagrams. Based on the solubility data, the technique of a new cleaner process for manufacturing chromium trioxide and potassium nitrate simultaneously by decomposing potassium dichromate with nitric acid was evaluated.

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1. Introduction

Chromium compounds are important basic chemicals essential to many industries. In the traditional manufacturing process based on the oxidation roasting of chromium ore with sodium carbonate and a large amount of limestone and dolomite additives at 1200 °C in a rotary kiln, the utilization efficiency of resources and energy is quite low. Especially, large amounts of chromium-containing toxic solid wastes and exhaust gas are discharged, resulting in serious worldwide pollution problems. Recently, a green manufacturing process for chromium compounds has been developed by the Institute of Process Engineering, Chinese Academy of Sciences.[1] With the design objective of eliminating pollution at the source, the green process achieves higher resource utilization efficiency and zero emission of chromium-containing waste residue.

Chromium trioxide is one species of the chromium compounds whose consumption occupies nearly 60% of that of all chromium derivative products. Concerning the industrial manufacturing of chromium trioxide, most reports and recent patents are on decomposing sodium dichromate with sulfuric acid. However, when manufacturing potassium chromium compounds, it is difficult to recycle both sodium ions and potassium ions inside the system. Therefore, manufacturing chromium trioxide by decomposing potassium dichromate with nitric acid becomes an important part of the green process. The main reaction in manufacturing chromium is as follows:

$$K_2Cr_2O_7(s) + 2HNO_3(aq) \rightarrow 2CrO_3(s) + 2KNO_3(s) + H_2O$$

In strong acidic aqueous solution, two chromium trioxide molecules tend to associate with each other and combine with one water molecule, which becomes $H_2Cr_2O_7$. Therefore, the five-component system $K_2Cr_2O_7 + CrO_3 + KNO_3 + HNO_3 + H_2O$ can be thought of as a reciprocal system which comprises double positive ions, K^+ and H^+, and double anions, $Cr_2O_7^{2-}$ and NO_3^-. The phase diagram for the system provides the theoretical basis for the manufacturing process above.

Some previous studies have been made on the solubility for the subsystems of the reciprocal system: $KNO_3 + HNO_3 + H_2O$, $CrO_3 + HNO_3 + H_2O$;[2,3] $K_2Cr_2O_7 + KNO_3 + H_2O$;[4,5] $K_2O + CrO_3 + H_2O$.[6] However, the study of the phase equilibrium for the reciprocal system $K_2Cr_2O_7 + CrO_3 + KNO_3 + HNO_3 + H_2O$ has not been reported so far. This paper reports the solubility data of this system at 0 °C, 25 °C, and 45 °C, and an evaluation of a new process for manufacturing chromium trioxide is also given.

2. Experimental Section

Apparatus and Reagents. A HZS-H type thermostat with an uncertainty of 0.1 °C was used for the 25 °C and 45 °C measurements. A refrigerator was used for 0 °C measurements. A 200 μL sampler and a precision balance with an uncertainty of 0.001 g were used for density measurement. A Rigaku D/max-2400 X-ray diffraction analyzer was used for solid-phase X-ray diffraction analysis.

The chemicals used were of analytical grade and were purchased from Beijing Chemical Plant: potassium dichromate (99% purity), chromium trioxide (99.9% purity), potassium nitrate (99.7% purity), nitric acid (65−68% on a mass percent basis), and fuming nitric acid (≥95% purity).

Experimental Method. The experiments were performed according to the following procedures: (a) Various concentrated supersaturated ternary solutions of $KNO_3 + HNO_3 + H_2O$ were prepared in which the mass of potassium nitrate was a little bit more than that in a saturated solution. (b) Potassium dichromate crystals and chromium trioxide crystals were added gradually into the supersaturated ternary solution. The mixtures were then put into a sealed tube in the thermostat and stirred for a period of time with the temperature controlled to (25 ± 0.1) °C or (45 ± 0.1) °C. Sampling was performed at 2 h intervals until equilibrium was attained. If two analyses gave identical results, it was assumed that equilibrium had been reached. For convenience, the samples were always agitated for 24 h and then allowed to stand for 24 h, which can definitely ensure that the system achieves equilibrium and enable all the suspended crystals to settle. The equilibrium of the 0 °C sample was achieved by agitation in a vibrator at (25 ± 0.1) °C for 24 h and then standing in the refrigerator at 0 °C for 24 h. (c) After equilibrium, liquid phases were taken out and analyzed. To obtain the water content of the solutions (the moles of water per 100 mol of dry salt), densities of the equilibrium solutions were calculated by weighing 200 μL samples on a precision

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Table 1. Solubility Data of the $K_2Cr_2O_7$ (1) + CrO_3 (2) + KNO_3 (3) + HNO_3 (4) + H_2O (5) System at 45 °C

	composition of liquid phase				
no.	$\frac{100[H^+]}{[H^+]+[K^+]}$	$\frac{100((1/2)[Cr_2O_7^{2-}])}{(1/2)[Cr_2O_7^{2-}]+[NO_3^-]}$	mol H_2O/ 100 mol dry salt	ρ/(kg·dm^{-3})	equilibrium solid phase
A	0	0	751	1.534	KNO_3
B	100	0			
C	100	100	367	1.584	$H_2Cr_2O_7(CrO_3)$
D	0	100	2666	1.131	$K_2Cr_2O_7$
E_1	66.03	0	13	1.481	KNO_3
E_2	58.90	100	960	1.454	$K_2Cr_2O_7 + K_2Cr_3O_{10}$
1	59.24	62.34	524	1.513	$K_2Cr_2O_7 + K_2Cr_3O_{10}$
2	64.25	51.07	393	1.622	$K_2Cr_2O_7 + K_2Cr_3O_{10}$
P_1	68.17	44.2	292	1.598	$K_2Cr_2O_7 + K_2Cr_3O_{10} + KNO_3$
3	70.61	43.70	309	1.645	$K_2Cr_2O_7 + K_2Cr_3O_{10}$
4	79.01	24.54	216	1.608	$K_2Cr_2O_7 + K_2Cr_3O_{10}$
5	100	0.34	77	1.670	$K_2Cr_2O_7 + K_2Cr_3O_{10}$
E_3	64.10	100	805	1.502	$K_2Cr_3O_{10} + K_2Cr_4O_{13}$
6	65.02	88.23	561	1.647	$K_2Cr_3O_{10} + K_2Cr_4O_{13}$
7	64.87	60.27	453	1.609	$K_2Cr_3O_{10} + K_2Cr_4O_{13}$
8	65.72	46.39	345	1.660	$K_2Cr_3O_{10} + K_2Cr_4O_{13}$
E_4	70	100	590	1.533	$K_2Cr_4O_{13} + H_2Cr_2O_7(CrO_3)$
9	67.49	89.55	514	1.505	$K_2Cr_4O_{13} + H_2Cr_2O_7(CrO_3)$
10	72.73	50.98	333	1.522	$K_2Cr_4O_{13} + H_2Cr_2O_7(CrO_3)$
11	82.72	26.54	245	1.486	$K_2Cr_4O_{13} + H_2Cr_2O_7(CrO_3)$
E_5	0	14.13	655	1.301	$K_2Cr_2O_7 + KNO_3$
12	1.22	17.13	670	1.304	$K_2Cr_2O_7 + KNO_3$
13	41.16	34.90	612	1.646	$K_2Cr_2O_7 + KNO_3$
14	61.97	51.87	386	1.519	$K_2Cr_2O_7 + KNO_3$
15	65.72	46.39	345	1.491	$K_2Cr_2O_7 + KNO_3$
16	68.23	31.09	287	1.518	$K_2Cr_2O_7 + KNO_3$
17	69.96	17.78	214	1.558	$K_2Cr_2O_7 + KNO_3$
18	71.87	15.02	194	1.680	$K_2Cr_2O_7 + KNO_3$
19	70.93	9.12	68	1.570	$K_2Cr_2O_7 + KNO_3$
20	68.70	5.39	67	1.772	$K_2Cr_2O_7 + KNO_3$
21	66.03	0	13	1.632	$K_2Cr_2O_7 + KNO_3$

Table 2. Solubility Data of the $K_2Cr_2O_7$ (1) + CrO_3 (2) + KNO_3 (3) + HNO_3 (4) + H_2O (5) System at 25 °C

	composition of liquid phase				
no.	$\frac{100[H^+]}{[H^+]+[K^+]}$	$\frac{100((1/2)[Cr_2O_7^{2-}])}{(1/2)[Cr_2O_7^{2-}]+[NO_3^-]}$	mol H_2O/100 mol dry salt	ρ/(kg·dm^{-3})	equilibrium solid phase
A	0	0	1450	1.216	KNO_3
B	100	0			
C	100	100	360	1.650	$H_2Cr_2O_7(CrO_3)$
D	0	100	3727	1.105	$K_2Cr_2O_7$
E_1	72.80	0	0	1.477	KNO_3
E_2	85.28	100	880	1.371	$K_2Cr_2O_7 + K_2Cr_3O_{10}$
1	83.10	62.35	481	1.413	$K_2Cr_2O_7 + K_2Cr_3O_{10}$
2	78.31	38.65	411	1.419	$K_2Cr_2O_7 + K_2Cr_3O_{10}$
P_1	77.34	21.44	316	1.338	$K_2Cr_2O_7 + K_2Cr_3O_{10} + KNO_3$
3	79.10	10.43	231	1.433	$K_2Cr_2O_7 + K_2Cr_3O_{10}$
4	82.40	7.63	187	1.421	$K_2Cr_2O_7 + K_2Cr_3O_{10}$
5	85.37	4.66	137	1.467	$K_2Cr_2O_7 + K_2Cr_3O_{10}$
E_3	94.55	100	520	1.401	$K_2Cr_3O_{10} + K_2Cr_4O_{13}$
6	94.34	85.30	391	1.447	$K_2Cr_3O_{10} + K_2Cr_4O_{13}$
7	88.67	58.12	337	1.512	$K_2Cr_3O_{10} + K_2Cr_4O_{13}$
8	84.57	29.19	310	1.504	$K_2Cr_3O_{10} + K_2Cr_4O_{13}$
E_4	97.91	100	370	1.417	$K_2Cr_4O_{13} + H_2Cr_2O_7(CrO_3)$
9	99.14	85.43	292	1.647	$K_2Cr_4O_{13} + H_2Cr_2O_7(CrO_3)$
10	97.71	56.12	271	1.603	$K_2Cr_4O_{13} + H_2Cr_2O_7(CrO_3)$
11	92.63	24.79	238	1.565	$K_2Cr_4O_{13} + H_2Cr_2O_7(CrO_3)$
12	85.37	4.66	137	1.508	$K_2Cr_4O_{13} + H_2Cr_2O_7(CrO_3)$
E_5	0	13.60	655	1.241	$K_2Cr_2O_7 + KNO_3$
13	6.32	12.20	903	1.250	$K_2Cr_2O_7 + KNO_3$
14	20.58	12.68	943	1.109	$K_2Cr_2O_7 + KNO_3$
15	38.37	16.72	983	1.265	$K_2Cr_2O_7 + KNO_3$
16	58.37	31.79	916	1.266	$K_2Cr_2O_7 + KNO_3$
17	69.13	31.35	748	1.312	$K_2Cr_2O_7 + KNO_3$
18	77.09	20.41	426	1.438	$K_2Cr_2O_7 + KNO_3$
19	77.72	15.94	249	1.506	$K_2Cr_2O_7 + KNO_3$
20	75.51	5.08	166	1.695	$K_2Cr_2O_7 + KNO_3$
21	73.38	2.22	99	1.614	$K_2Cr_2O_7 + KNO_3$

balance. (d) Solid phases were separated by filtration at the corresponding constant temperature. One part of the solid phases was dissolved into water and analyzed by chemical methods. The other part was dried at room

Table 3. Solubility Data of the $K_2Cr_2O_7$ (1) + CrO_3 (2) + KNO_3 (3) + HNO_3 (4) + H_2O (5) System at 0 °C

	composition of liquid phase				
no.	$\frac{100[H^+]}{[H^+]+[K^+]}$	$\frac{100((1/2)[Cr_2O_7^{2-}])}{(1/2)[Cr_2O_7^{2-}]+[NO_3^-]}$	mol H_2O/100 mol dry salt	ρ/(kg·dm^{-3})	equilibrium solid phase
A	0	0	4218	1.044	KNO_3
B	100	0			
C	100	100	899	1.665	$H_2Cr_2O_7(CrO_3)$
D	0	100	18197	1.032	$K_2Cr_2O_7$
E_1	70.90	0	0	1.453	KNO_3
E_2	95.79	100	1254	1.376	$K_2Cr_2O_7 + H_2Cr_2O_7(CrO_3)$
1	90.06	49.69	641	1.433	$K_2Cr_2O_7 + H_2Cr_2O_7(CrO_3)$
2	86.80	26.48	438	1.263	$K_2Cr_2O_7 + H_2Cr_2O_7(CrO_3)$
3	89.12	20.96	252	1.308	$K_2Cr_2O_7 + H_2Cr_2O_7(CrO_3)$
4	85.51	1.55	134	1.474	$K_2Cr_2O_7 + H_2Cr_2O_7(CrO_3)$
5	88.87	0.45	118	1.586	$K_2Cr_2O_7 + H_2Cr_2O_7(CrO_3)$
6	100	0.05	80	1.652	$H_2Cr_2O_7(CrO_3)$
E_3	0	7.79	3868	1.111	$K_2Cr_2O_7 + KNO_3$
7	17.11	7.97	3522	1.113	$K_2Cr_2O_7 + KNO_3$
8	81.63	32.93	780	1.263	$K_2Cr_2O_7 + KNO_3$
9	82.82	25.56	395	1.308	$K_2Cr_2O_7 + KNO_3$
P_1	84.83	15.11	339	1.194	$K_2Cr_2O_7 + H_2Cr_2O_7(CrO_3) + KNO_3$
10	84.87	6.85	283	1.474	$K_2Cr_2O_7 + KNO_3$
11	79.07	2.20	178	1.544	$K_2Cr_2O_7 + KNO_3$
12	76.58	1.26	152	1.604	$K_2Cr_2O_7 + KNO_3$
13	70.89	0.30	37	1.752	$K_2Cr_2O_7 + KNO_3$

temperature, pestled into powder, and then analyzed by X-ray diffraction.

Analytical Method. $Cr_2O_7^{2-}$ was titrated by using *N*-phenylanthranilic acid as the indicator (uncertainty of 0.08 mass %). K^+ was determined by gravimetric analysis with sodium tetraphenylboron (uncertainty of 0.05 mass %). The total amount of acid was analyzed by neutralization titration with sodium hydrate (uncertainty of 0.10 mass %). Notably, when sodium hydroxide was titrated into the solution, the reaction $Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$ took place, and since the hydroxyl consumed was included in the acidity measurement, the molality of H^+ should be corrected by subtracting the 2-fold Cr^{6+} molality from the experimental total H^+ molality amount.

3. Results and Discussion

The solubility data of the $K_2Cr_2O_7$ + CrO_3 ($H_2Cr_2O_7$) + KNO_3 + HNO_3 + H_2O system at 45 °C, 25 °C, and 0 °C were determined and are presented in Tables 1−3, respectively. The phase diagrams are plotted in Figures 1−3, respectively.

The phase diagrams of the reciprocal system were established according to a universal projection drawing method.[7] The ordinates of the lateral projection drawings, Figures 1a, 2a, and 3a, represent the moles of water per 100 mol of dry salt in solution (water index). Figures 1b, 2b, and 3b are named vertical projection drawings of the phase diagrams (dry salt diagrams), which reflect the projections of spatial cosaturation composition lines on which at least two solid phases deposit from the solution. The abscissas express the mole fractions of H^+ in cations, and the vertical coordinates express the mole fractions of $Cr_2O_7^{2-}$ in anions.

Figures 1−3 show that the system contains a total of five solid species: $K_2Cr_2O_7$, $H_2Cr_2O_7$ (CrO_3), $K_2Cr_3O_{10}$, $K_2Cr_4O_{13}$, and KNO_3. The corners A, C, and D represent the pure crystals of KNO_3, $H_2Cr_2O_7$, and $K_2Cr_2O_7$, respectively; points A′, C′, and D′ represent the corresponding binary saturated aqueous solution; and the corner B represents the hypothetical pure HNO_3 solid, which does not exist. Points E_1 represent the component of the saturated ternary solution KNO_3 + HNO_3 + H_2O at the highest nitric acid concentration at each temperature.

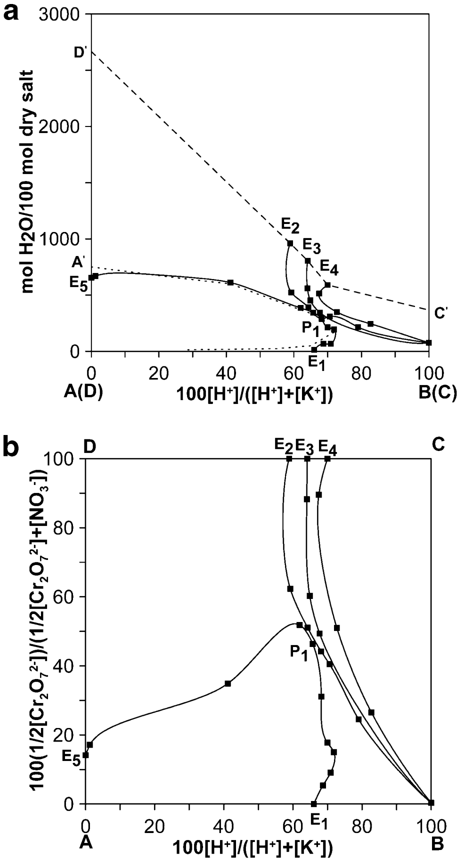

Figure 1. (a) AB(CD) lateral projection drawing of the phase diagram of the $K_2Cr_2O_7$ (1) + CrO_3 (2) + KNO_3 (3) + HNO_3 (4) + H_2O (5) system at 45 °C. A, KNO_3; B, HNO_3; C, (1/2)$H_2Cr_2O_7$; D, (1/2)$K_2Cr_2O_7$. ■, Experiment point; solid line, cosaturation composition line of two salts; dashed line, equilibrium composition line of $K_2Cr_2O_7$ (1) + CrO_3 (2) + H_2O (5) (ref 6); dotted line, equilibrium composition line of KNO_3 (3) + HNO_3 (4) + H_2O (5) (ref 3). (b) Vertical projection drawing of the phase diagram of the $K_2Cr_2O_7$ (1) + CrO_3 (2) + KNO_3 (3) + HNO_3 (4) + H_2O (5) system at 45 °C.

In Figures 1 and 2, points E_2, E_3, and E_4 represent respectively the equilibrium of two solid phases at the extreme of the corresponding side CD and point E_5 repre-

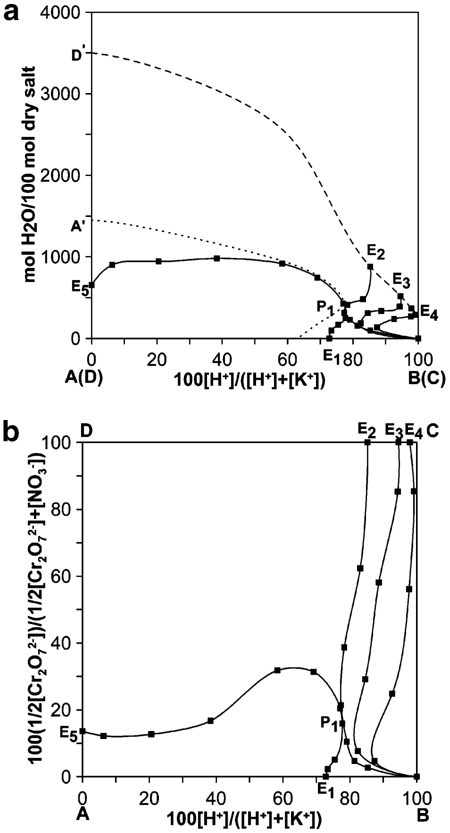

Figure 2. (a) AB(CD) lateral projection drawing of the phase diagram of the $K_2Cr_2O_7$ (1) + CrO_3 (2) + KNO_3 (3) + HNO_3 (4) + H_2O (5) system at 25 °C. (b) Vertical projection drawing of the phase diagram of the $K_2Cr_2O_7$ (1) + CrO_3 (2) + KNO_3 (3) + HNO_3 (4) + H_2O (5) system at 25 °C.

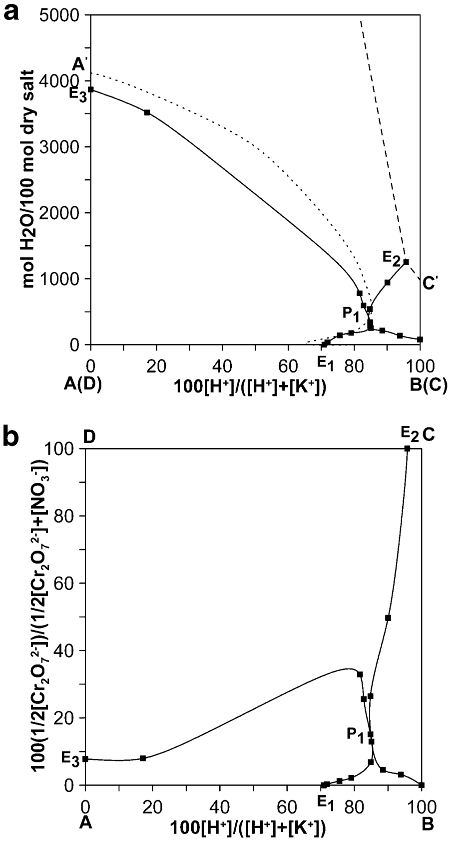

Figure 3. (a) AB(CD) lateral projection drawing of the phase diagram of the $K_2Cr_2O_7$ (1) + CrO_3 (2) + KNO_3 (3) + HNO_3 (4) + H_2O (5) system at 0 °C. (b) Vertical projection drawing of the phase diagram of the $K_2Cr_2O_7$ (1) + CrO_3 (2) + KNO_3 (3) + HNO_3 (4) + H_2O (5) system at 0 °C.

sents the equilibrium of $K_2Cr_2O_7$ and KNO_3 in the ternary solution. Point P_1 is the isothermal invariant point, which represents the equilibrium of three solid phases $K_2Cr_2O_7$, $K_2Cr_3O_{10}$, and KNO_3. In Figure 3, point E_2 represents the equilibrium of two solid phases $K_2Cr_2O_7$ and $H_2Cr_2O_7$ and point E_3 represents the equilibrium of $K_2Cr_2O_7$ and KNO_3 in the ternary solution. Point P_1 represents the equilibrium of three solid phases $K_2Cr_2O_7$, $H_2Cr_2O_7$ (CrO_3), and KNO_3.

The crystallization zones of $H_2Cr_2O_7$ (CrO_3) and KNO_3 at the diagonal vertexes do not connect to each other when the system temperature is set at 25 °C or 45 °C, which means that solid phases consisting of these two compounds respectively cannot exist simultaneously in the solution. These two salts are an unstable salt pair. However, $H_2Cr_2O_7$ (CrO_3) is inclined to precipitate at high nitric acid concentration while KNO_3 tends to deposit at lower nitric acid concentration, which provides the theoretical basis for separating them. The solubility of $K_2Cr_2O_7$ is relatively small due to the fact that its crystallization zone is much greater than those of KNO_3 and $H_2Cr_2O_7$ (CrO_3). It easily precipitates with KNO_3 or $H_2Cr_2O_7$ (CrO_3). Therefore, the refining procedure of product CrO_3 and byproduct KNO_3 seems to be particularly important.

Also, with the temperature decreasing from 45 °C to 0 °C, the crystallization zones of KNO_3 and $H_2Cr_2O_7$ (CrO_3) shrink considerably. Although the solubility of single $H_2Cr_2O_7$ (CrO_3) does not vary much with the change of temperature, the solubility of $K_2Cr_2O_7$ and KNO_3 change considerably, which leads to the comparative variation of crystallization zones. When the system temperature is controlled at 45 °C and 25 °C, $K_2Cr_2O_7$ and CrO_3 deposit in a large amount at a certain HNO_3 concentration and they combine with each other in various proportions, consequently forming crystals of $K_2Cr_3O_{10}$ and $K_2Cr_4O_{13}$ when the mole ratio of deposited $H_2Cr_2O_7$ to $K_2Cr_2O_7$ is larger than a certain value, which varies with the temperature. For 45 °C, the value is 1.433, and for 25 °C, it is 5.79. However, when the system temperature is 0 °C, the amount of precipitated $K_2Cr_2O_7$ and CrO_3 is small, which greatly simplifies the analysis of the phase diagram. It can be concluded from the above figures that, besides adjusting HNO_3 concentration, adjusting temperature is another effective approach to separating CrO_3 and KNO_3. CrO_3 can be separated from a high nitric acid concentration (65−75% on a mass percent basis) solution at 45 °C, and KNO_3 can be extracted from a low nitric acid concentration (30−40% on a mass percent basis) solution at 0 °C.

4. Conclusion

The solubility data of the $K_2Cr_2O_7$ + CrO_3 ($H_2Cr_2O_7$) + KNO_3 + HNO_3 + H_2O system at 0 °C, 25 °C, and 45 °C were determined. According to the solubility data measured, the phase diagram was constructed, and analyses and discussions are made on the construction of the phase diagram. Separating CrO_3 and KNO_3 through adjusting HNO_3 concentration and temperature makes it feasible to manufacture chromium trioxide and potassium nitrate simultaneously by decomposing potassium dichromate with nitric acid in the new green process.

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