# Study on the $KOH + K_2CrO_4 + K_2CO_3 + H_2O$ System

**Jin-lan Cui* and Yi Zhang**

Institute of Chemical Metallurgy, Chinese Academy of Sciences, Zhongguancun, P.O. Box 353, Beijing 100080, People's Republic of China

The phase equilibrium data for the quaternary system $KOH + K_2CrO_4 + K_2CO_3 + H_2O$ between 20 °C and 80 °C were measured, and the phase diagram was constructed. Simultaneously, concentration of $K_2CrO_4$ in aqueous solution of KOH was compared with that in aqueous solution of KOH saturated with $K_2CO_3$. Furthermore, analyses and discussions are made on the crystalline areas in the phase diagram.

## Introduction

An original conversion process for potassium chromate was proposed by the Institute of Chemical Metallurgy, Chinese Academy of Sciences, whose main technological process is oxidization and dilution, followed by separation. In the dilution process, the suitable concentration of KOH needs to be controlled to achieve high-quality products and a high percent recovery of effective components. In addition, the order of salting out and the separation-out amount of the solid phase are also some very important parameters in the process design. The phase diagram for the system $KOH + K_2CrO_4 + K_2CO_3 + H_2O$ is requested for the determination of the parameters above.

Some studies[1−3] have been done on the solubility for the subsystems of the quaternary system $KOH + K_2CrO_4 + K_2CO_3 + H_2O$, but the study of the phase equilibrium for the quaternary system $KOH + K_2CrO_4 + K_2CO_3 + H_2O$ has not been reported so far.

In this paper, the phase equilibrium for the quaternary system listed above is studied.

## Experimental Section

***Apparatus and Reagents.*** A HZQ-C type thermostated vibrator with a precision of 0.1 °C was used for the equilibrium measurement. A SIEMENS D500 X-ray diffraction analyzer was used for solid-phase X-ray diffraction analysis.

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

***Experimental Method.*** The solubility was determined employing the method of isothermal solution saturation. The experimental systems prepared according to specified component ratio were placed in the thermostated vibrator. The experiments were performed at ambient pressure, and the temperature was fixed at four specific points: 20 °C, 40 °C, 60 °C, and 80 °C. The equilibrium was achieved by agitation for 24 h. After equilibrium, stirring was discontinued and the solids were sedimented. The time of clarification was about 8 h. Next, a sample was removed and analyzed. $CrO_4^{2-}$ was titrated by using *N*-phenylanthranilic acid solution as indicator (precision: <0.1 mass %). $OH^-$ and $CO_3^{2-}$ were determined by hydrochloric acid solution using phenolphthalein solution and methyl orange solution as the indicators, respectively (precision: <0.6 mass %), and $K^+$ was analyzed by a gravimetric method (precision: <0.5 mass %). The equilibrium solid phase was dried in a desiccator at room temperature and then determined by an X-ray diffraction method with a SIEMENS D500 X-ray diffraction analyzer.

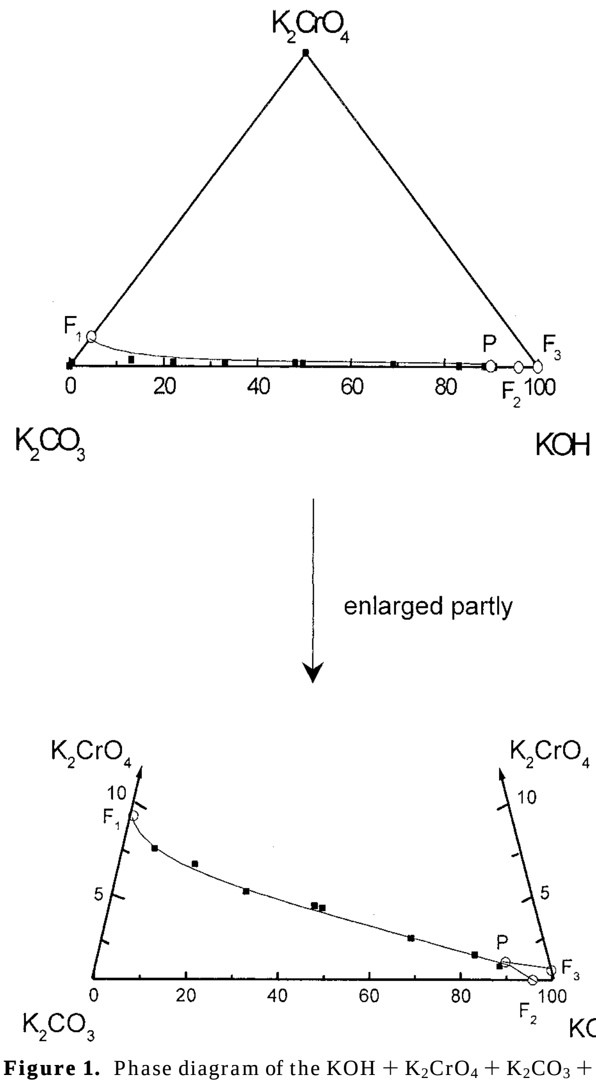


**Figure 1.** Phase diagram of the $KOH + K_2CrO_4 + K_2CO_3 + H_2O$ system at 80 °C.

* To whom correspondence should be addressed. E-mail: cuijl@hotmail.com.

10.1021/je0001734 CCC: $19.00 
Published on Web 10/25/2000

**Table 1. Solubility Data of the KOH + $K_2CrO_4$ + $K_2CO_3$ + $H_2O$ System**

| composition of liquid phase, g/100 g of dry salt | | | | |
|---|---|---|---|---|
| KOH | $K_2CrO_4$ | $K_2CO_3$ | $H_2O$ | equilibrium solid phase |
| | | | $t = 20$ °C | |
| 9.02 | 0.68 | 90.30 | 80.60 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 19.70 | 0.67 | 79.63 | 91.67 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 33.00 | 0.52 | 66.48 | 88.60 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 49.67 | 0.46 | 49.87 | 99.49 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 71.11 | 0.28 | 28.61 | 94.28 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 83.70 | 0.20 | 16.10 | 95.53 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 88.50 | 0.11 | 11.39 | 93.60 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 92.37 | 0.07 | 7.56 | 88.68 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 96.33 | 0.03 | 3.64 | 71.33 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 97.353 | 0.068 | 2.579 | 91.85 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ + $KOH·2H_2O$ |
| 0 | 4.05 | 95.95 | | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 97.78 | 0 | 2.22 | | $K_2CO_3·1.5H_2O + KOH·2H_2O$ |
| 99.992 | 0.008 | 0 | | $K_2CrO_4 + KOH·2H_2O$ |
| | | | $t = 40$ °C | |
| 7.87 | 0.78 | 91.35 | 70.01 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 16.57 | 0.65 | 82.78 | 73.20 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 30.94 | 0.60 | 68.46 | 78.21 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 48.50 | 0.56 | 50.94 | 89.61 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 63.99 | 0.42 | 35.59 | 87.25 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 77.55 | 0.31 | 22.14 | 87.64 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 87.52 | 0.16 | 12.32 | 89.69 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 89.34 | 0.009 | 10.651 | 78.95 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 92.35 | 0.002 | 7.648 | 50.48 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 95.33 | 0.09 | 4.58 | 75.70 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ + $KOH·2H_2O$ |
| 0 | 5.94 | 94.06 | | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 96.63 | 0 | 3.37 | | $K_2CO_3·1.5H_2O + KOH·2H_2O$ |
| 99.983 | 0.017 | 0 | | $K_2CrO_4 + KOH·2H_2O$ |
| | | | $t = 60$ °C | |
| 7.77 | 0.93 | 91.30 | 69.83 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 24.76 | 0.84 | 74.40 | 86.78 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 33.14 | 0.64 | 66.22 | 80.04 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 42.97 | 0.62 | 56.41 | 83.45 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 63.32 | 0.52 | 36.16 | 76.41 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 74.91 | 0.35 | 24.75 | 84.20 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 85.69 | 0.12 | 14.19 | 74.76 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 89.42 | 0.04 | 10.54 | 63.70 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 91.05 | 0.02 | 8.93 | 65.87 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 92.88 | 0.13 | 6.99 | 104.41 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ + $KOH·2H_2O$ |
| 0 | 7.75 | 92.25 | | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 96.14 | 0 | 3.86 | | $K_2CO_3·1.5H_2O + KOH·2H_2O$ |
| 99.95 | 0.05 | 0 | | $K_2CrO_4 + KOH·2H_2O$ |
| | | | $t = 80$ °C | |
| 12.13 | 1.94 | 85.93 | 87.38 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 21.40 | 1.22 | 77.38 | 86.82 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 32.60 | 0.94 | 66.46 | 77.33 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 47.58 | 0.90 | 51.52 | 105.92 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 49.23 | 0.88 | 49.89 | 106.56 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 68.85 | 0.56 | 30.59 | 109.76 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 82.98 | 0.27 | 16.75 | 82.90 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 88.51 | 0.14 | 11.35 | 76.54 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 89.36 | 0.05 | 10.59 | 60.58 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 89.78 | 0.19 | 10.03 | 87.12 | $K_2CrO_4 + K_2CO_3·1.5H_2O$ + $KOH·2H_2O$ |
| 0 | 9.27 | 90.73 | | $K_2CrO_4 + K_2CO_3·1.5H_2O$ |
| 95.87 | 0 | 4.13 | | $K_2CO_3·1.5H_2O + KOH·2H_2O$ |
| 99.90 | 0.10 | 0 | | $K_2CrO_4 + KOH·2H_2O$ |

## Results and Discussions

***Quaternary System KOH + $K_2CrO_4$ + $K_2CO_3$ + $H_2O$.*** The solubility data for the quaternary system KOH + $K_2CrO_4$ + $K_2CO_3$ + $H_2O$ between 20 °C and 80 °C were measured and are presented in Table 1. The phase diagram at 80 °C is plotted in Figure 1, and those at 20 °C, 40 °C, and 60 °C are similar to that in Figure 1.

Figure 1 shows that the system has three crystallization zones, the $K_2CrO_4$ crystallization zone, the $K_2CO_3·1.5H_2O$ crystallization zone, and the $KOH·2H_2O$ crystallization zone. Among them the crystallization zone of $K_2CrO_4$ is far larger than those of the others, which means that potassium chromate is very easily separated out from the system when the amount of water is suitable. The result provides the theoretical basis for the separation-out of potassium chromate from the reaction system.

Point P is an invariant point. Points $F_1$, $F_2$, and $F_3$ represent respectively the equilibrium of the solid phases at the two extremes of the corresponding side.

**Table 2. Comparison of Solubility of $K_2CrO_4$ in KOH Aqueous Solution with That in KOH Aqueous Solution Saturated with $K_2CO_3$ at 40 °C**

| in aqueous solution of KOH without $K_2CO_3$ in coexistence, $c$/g·L$^{-1}$ | | in aqueous solution of KOH saturated with $K_2CO_3$, $c$/g·L$^{-1}$ | |
|---|---|---|---|
| KOH | $K_2CrO_4$ | KOH | $K_2CrO_4$ |
| 22.38 | 494.55 | 69.94 | 6.95 |
| 71.94 | 397.64 | 143.88 | 5.60 |
| 114.57 | 312.01 | 255.79 | 4.93 |
| 133.22 | 270.52 | 379.69 | 4.37 |
| 193.17 | 177.57 | 495.59 | 3.29 |
| 227.81 | 141.05 | 603.50 | 2.39 |
| 269.78 | 104.56 | 699.43 | 1.31 |
| 319.74 | 54.34 | 763.37 | 0.75 |
| 331.73 | 43.13 | 927.24 | 0.07 |
| 783.36 | 0.93 | | |
| 879.28 | 0.30 | | |

**Table 3. Comparison of Solubility of $K_2CrO_4$ in KOH Aqueous Solution with That in KOH Aqueous Solution Saturated with $K_2CO_3$ at 80 °C**

| in aqueous solution of KOH without $K_2CO_3$ in coexistence, $c$/g·L$^{-1}$ | | in aqueous solution of KOH saturated with $K_2CO_3$, $c$/g·L$^{-1}$ | |
|---|---|---|---|
| KOH | $K_2CrO_4$ | KOH | $K_2CrO_4$ |
| 27.98 | 565.91 | 97.52 | 15.61 |
| 115.11 | 376.17 | 174.26 | 9.93 |
| 122.57 | 365.11 | 273.38 | 7.88 |
| 245.13 | 188.51 | 350.11 | 6.65 |
| 273.11 | 154.01 | 361.71 | 6.31 |
| 399.67 | 59.75 | 487.60 | 3.99 |
| 439.64 | 40.26 | 682.64 | 2.20 |
| 479.61 | 23.56 | 767.37 | 1.19 |
| 511.58 | 15.20 | 871.28 | 0.30 |
| 799.34 | 2.35 | | |
| 879.28 | 0.90 | | |

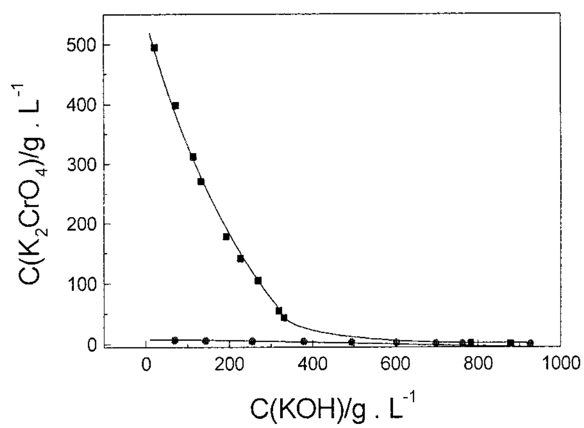


**Figure 2.** Solubility isotherms of $K_2CrO_4$ at 40 °C: ■, in KOH aqueous solution; ●, in KOH aqueous solution saturated with $K_2CO_3$.

***Comparison of Solubility of $K_2CrO_4$ in Aqueous Solution of KOH with That in Aqueous Solution of KOH Saturated with $K_2CO_3$.*** Solubility data of $K_2CrO_4$

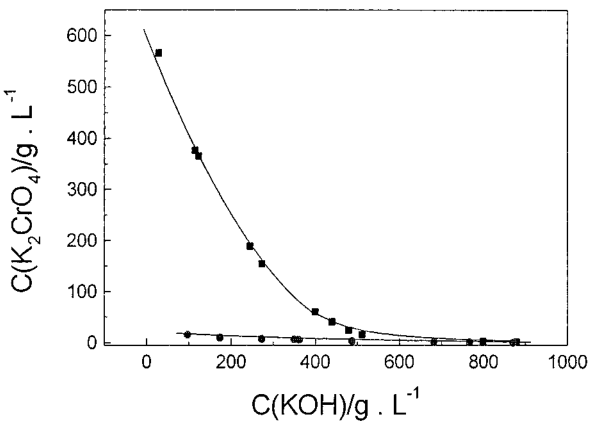


**Figure 3.** Solubility isotherms of $K_2CrO_4$ at 80 °C: ■, in KOH aqueous solution; ●, in KOH aqueous solution saturated with $K_2CO_3$.

in the KOH aqueous solution and in the KOH aqueous solution saturated with $K_2CO_3$ at 40 °C and 80 °C were respectively presented in Tables 2 and 3. The corresponding isotherms are plotted in Figures 2 and 3.

It is concluded that, by analyzing Tables 2 and 3 and Figures 2 and 3, the concentration of potassium chromate declines sharply because of adding $K_2CO_3$ into the KOH + $K_2CrO_4$ + $H_2O$ system. That is, the salting out effect of $K_2CO_3$ to $K_2CrO_4$ is very strong. There are similar results at 20 °C and 60 °C. The result indicates that it is beneficial to precipitate $K_2CrO_4$ crystals from the KOH + $K_2CrO_4$ + $H_2O$ system with saturated $K_2CO_3$ in coexistence. The result is in good accordance with that reached by analyzing the phase diagram of the KOH + $K_2CrO_4$ + $K_2CO_3$ + $H_2O$ system.

## Conclusion

Phase equilibria for the quaternary system KOH + $K_2CrO_4$ + $K_2CO_3$ + $H_2O$ between 20 °C and 80 °C were studied. From the solubility results, the phase diagram was plotted, and the solubility isotherms of $K_2CrO_4$ in the KOH aqueous solutions and in the KOH aqueous solutions saturated with $K_2CO_3$ were plotted.

The studies in the paper lay a foundation for determining the parameters requested for the new production technology of potassium chromate.

## Literature Cited


(1) Lang, A. A.; Sukava, A. J. The System KOH−$K_2CO_3$−$H_2O$ at Low Temperatures. *Can. J. Chem.* **1958**, *36*, 1064−1069.

(2) Hoštálek, Z.; Kašparová, I. Ternární Soustava Voda-Uhličitan Draselný-Hydroxyd Draselný. *Chem. Listy* **1956**, *50*, 979−981.

(3) Carbonnel, L. Le Système ternaire Eau-Potasse-Carbonate de Potassium.-Étude Dans L'intervalle de Température −22 °C, +30.7 °C. *Bull. Soc. Chim. Fr.* **1959**, *11*, 1990−1996.



Received for review June 12, 2000. Accepted September 11, 2000. This project was supported by the Chinese Academy of Sciences (No. KZ95T-05) and the National Natural Science Foundation of China (No. 59674022).

JE0001734