44 *J. Chem. Eng. Data* **2007,** *52,* 44−46

# (Solid + Liquid) Phase Diagram for the Ternary Potassium Oxalate + Hydrogen Peroxide + Water System at 283.15 K and 293.15 K

**Hong-Kun Zhao,* Dao-Sen Zhang, Cao Tang, Rong-Rong Li, Wen-Lin Xu, and Ya-Qiong Wang**

College of Chemistry & Chemical Engineering, YangZhou University, YangZhou, Jiangsu 225002, People's Republic of China

---

The solubility and density of the equilibrium liquid phase for the ternary $K_2C_2O_4 + H_2O_2 + H_2O$ system were determined experimentally at (283.15 and 293.15) K. The phase diagrams of the system were constructed based on the measured solubility. The compound $K_2C_2O_4 \cdot H_2O_2$ was confirmed by Schreinemaker's wet residues method. At (283.15 and 293.15) K, two solid phases were formed in the ternary $K_2C_2O_4 + H_2O_2 + H_2O$ system that correspond to $K_2C_2O_4 \cdot H_2O$ and $K_2C_2O_4 \cdot H_2O_2$. Results indicated that the phase diagrams of the ternary system are similar at different temperatures. The double salt $K_2C_2O_4 \cdot H_2O_2$ has a bigger crystallization field than either $K_2C_2O_4 \cdot H_2O$ or the mixture. The solubilities of $K_2C_2O_4 \cdot H_2O$ and $K_2C_2O_4 \cdot H_2O_2$ increase slightly with increasing temperature, while the crystalline region of the compound $K_2C_2O_4 \cdot H_2O_2$ decreases as the temperature increases.

---

## Introduction

Perhydrates are of considerable technical importance as carriers of hydrogen peroxide, several perhydrates such as $Na_2CO_3 \cdot 1.5H_2O_2$, $CO(NH_2)_2 \cdot H_2O_2$, $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$, etc. have been produced and used in industry. Pederson and Pederson[1] synthesized a new hydrogen peroxide adduct with potassium oxalate, with the formula $K_2C_2O_4 \cdot H_2O_2$ by the following approach: potassium oxalate monohydrate was dissolved in an aqueous hydrogen peroxide solution (30 % $H_2O_2$ in water). By slow evaporation at room temperature, crystals in the form of diamond-shaped plates separated out. The analytical results showed that the composition of the crystals very closely corresponds to $K_2C_2O_4 \cdot H_2O_2$. The crystal structure was determined from three-dimensional X-ray data.[1] The structure of $K_2C_2O_4 \cdot H_2O_2$ is closely related to the structure of potassium oxalate monohydrate. The oxalate ion is centrosymmetric and planar; the hydrogen peroxide molecules are engaged in relatively short hydrogen bonds of 2.591 ± 0.009 Å to oxalate oxygens in both directions, thus building a three-dimensional network constituting a relatively open but fairly stable structure. The potassium ions are eight-coordinated by oxalate and hydrogen peroxide oxygens. The mean K−O distance is 2.907 Å. In 1980, Adams et al. studied the thermal decomposition of $K_2C_2O_4 \cdot H_2O_2$ under isothermal conditions.[2] Nevertheless, to the best of our knowledge, other aspects of the adduct $K_2C_2O_4 \cdot H_2O_2$ have not been described elsewhere in the literature.

It is well-known that solid−liquid phase equilibrium data are important in crystallization processes. As described by Pederson and Pederson[1] and Adams et al.,[2] potassium oxalate reacts with hydrogen peroxide solution of a given concentration and $K_2C_2O_4 \cdot H_2O_2$ crystallizes from the system at a certain temperature. Obviously, the preparing process of $K_2C_2O_4 \cdot H_2O_2$ is based on the phase diagram of the ternary $K_2C_2O_4 + H_2O_2 + H_2O$ system. It is very important to study the system and construct the phase diagram of the ternary $K_2C_2O_4 + H_2O_2 + H_2O$ system. Although the phase diagram of the systems $Na_2CO_3 + H_2O_2 + H_2O$,[3] $CO(NH_2)_2 + H_2O_2 + H_2O$,[4] $Na_2SO_4 + H_2O_2 + H_2O$,[5] and $Na_2SO_4 + NaCl + H_2O_2 + H_2O$[6] have been investigated, we have found no data on the solubility or phase diagram for the $K_2C_2O_4 + H_2O_2 + H_2O$ system in the literature. The objective of this research is to generate and analyze the phase diagrams of a ternary system at (283.15 and 293.15) K by Schreinemaker's wet residues method[7] and demonstrate the temperature dependence of the ternary phase diagram.

## Experimental Section

***Materials.*** The hydrogen peroxide used (not containing stabilizers) was produced by the Jiangsu Yangnong Chemical Group Co. Ltd., with a mass fraction of 75 %. The potassium oxalate (purity of 99.96 %), produced by the Shanghai Dafeng Oxalic Acid Co. Ltd., was of reagent quality. The water used to prepare solutions was twice distilled ($<5\ \mu S \cdot cm^{-1}$ conductivity).

***Procedure.*** A thermostat was used in this experiment, with a device for rotating several bottles at a time. The schematics of experimental system is shown in Figure 1. The glass stoppers of the bottles were covered with rubber caps while in the thermostat.

A known mass of potassium oxalate 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 of the solution in the bottle became constant, it indicated that the equilibrium was achieved. Generally, it took about 6 h to reach equilibrium. After equilibrium was achieved, the solid and liquid phases were separated by filtration, and then both were analyzed. This procedure was repeated by varying the ratio of hydrogen peroxide and potassium oxalate in order to obtain different compositions of the solid and liquid phases. In this experiment, the mass of potassium oxalate was fixed while the mass and concentration of hydrogen peroxide varied.

---

* Corresponding author. E-mail: hkzhao@zzu.edu.cn. Tel: +86 514 7975568. Fax: +86 514 7975244.

10.1021/je060182y CCC: $37.00

**Figure 1.** Equipment of the experimental system.

**Table 1. Mass Fraction Solubilities and Densities Value of the Ternary System $K_2C_2O_4$ (1) + $H_2O_2$ (2) + $H_2O$ (3) at 283.15 K**[a]

| liquid phase | | moist solid phase | | density of liquid phase | |
|---|---|---|---|---|---|
| 100 $w_1$ | 100 $w_2$ | 100 $w_1$ | 100 $w_2$ | g·mL$^{-1}$ | solid phase |
| 24.17 | 0 | 88.47 | 0 | 1.1181 | $K_2C_2O_4\cdot H_2O$ |
| 24.21 | 1.52 | 82.24 | 0.69 | 1.1338 | $K_2C_2O_4\cdot H_2O$ |
| 24.35 | 2.46 | 79.76 | 8.78 | 1.1482 | $K_2C_2O_4\cdot H_2O$ + $K_2C_2O_4\cdot H_2O_2$ |
| 19.54 | 6.24 | 78.83 | 13.83 | 1.176 | $K_2C_2O_4\cdot H_2O_2$ |
| 18.94 | 13.17 | 79.71 | 16.29 | 1.1998 | $K_2C_2O_4\cdot H_2O_2$ |
| 23.52 | 20.22 | 68.95 | 17.32 | 1.2709 | $K_2C_2O_4\cdot H_2O_2$ |
| 26.53 | 26.63 | 81.23 | 16.97 | 1.3257 | $K_2C_2O_4\cdot H_2O_2$ |
| 27.97 | 32.31 | 80.89 | 16.93 | 1.3569 | $K_2C_2O_4\cdot H_2O_2$ |
| 30.54 | 35.22 | 80.26 | 17.60 | 1.4014 | $K_2C_2O_4\cdot H_2O_2$ |
| 33.9 | 38.99 | 58.55 | 28.78 | 1.4471 | $K_2C_2O_4\cdot H_2O_2$ |
| 36.67 | 43.09 | 74.21 | 22.48 | 1.4639 | $K_2C_2O_4\cdot H_2O_2$ |

[a] *w*, mass fraction.

***Analysis.*** The moist solid samples were dissolved in water, and aliquot portions of the solutions obtained were used for the analysis. The hydrogen peroxide concentration was determined by the iodometric method. The total concentration of the oxalate ion and the hydrogen peroxide concentration was measured by titrating the acidified solution with standard potassium permanganate. Then the oxalate ion concentration can be determined by subtracting the hydrogen peroxide concentration from the total concentration of the oxalate ion and hydrogen peroxide. The densities ($\rho$) were measured with a specific weighing bottle calibrated by the floating force of air with a precision of ± 0.2 mg. 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 %). In these studies, X-ray diffraction and infrared absorption spectroscopy were also employed to determine whether the solid phase was pure or a compound.

## Results and Discussion

The measured solubility and the density of the liquid phase for the ternary $K_2C_2O_4 + H_2O_2 + H_2O$ system at (283.15 and 293.15) K are shown in Tables 1 and 2, respectively. The ternary phase diagrams are given in Figures 2 and 3.

**Table 2. Mass Fraction Solubilities and Densities Value of the Ternary System $K_2C_2O_4$ (1) + $H_2O_2$ (2) + $H_2O$ (3) at 293.15 K**[a]

| liquid phase | | moist solid phase | | density of liquid phase | |
|---|---|---|---|---|---|
| 100 $w_1$ | 100 $w_2$ | 100 $w_1$ | 100 $w_2$ | g·mL$^{-1}$ | solid phase |
| 26.67 | 0 | 86.54 | 0 | 1.1193 | $K_2C_2O_4\cdot H_2O$ |
| 27.92 | 1.51 | 85.59 | 0.61 | 1.1405 | $K_2C_2O_4\cdot H_2O$ |
| 29.33 | 2.64 | 81.46 | 3.7 | 1.1591 | $K_2C_2O_4\cdot H_2O$ + $K_2C_2O_4\cdot H_2O_2$ |
| 23.9 | 7.21 | 84.05 | 14.31 | 1.1898 | $K_2C_2O_4\cdot H_2O_2$ |
| 21.24 | 12.41 | 83.66 | 15.81 | 1.2146 | $K_2C_2O_4\cdot H_2O_2$ |
| 21.76 | 19.87 | 77.49 | 16.93 | 1.2635 | $K_2C_2O_4\cdot H_2O_2$ |
| 23.82 | 25.48 | 79.47 | 17.22 | 1.3062 | $K_2C_2O_4\cdot H_2O_2$ |
| 28.3 | 31.74 | 80.58 | 17.63 | 1.3776 | $K_2C_2O_4\cdot H_2O_2$ |
| 33.01 | 35.43 | 82.03 | 18.24 | 1.4082 | $K_2C_2O_4\cdot H_2O_2$ |
| 39.32 | 38.72 | 78.28 | 19.53 | 1.4389 | $K_2C_2O_4\cdot H_2O_2$ |
| 42.73 | 40.88 | 75.81 | 21.11 | 1.4464 | $K_2C_2O_4\cdot H_2O_2$ |

[a] *w*, mass fraction.

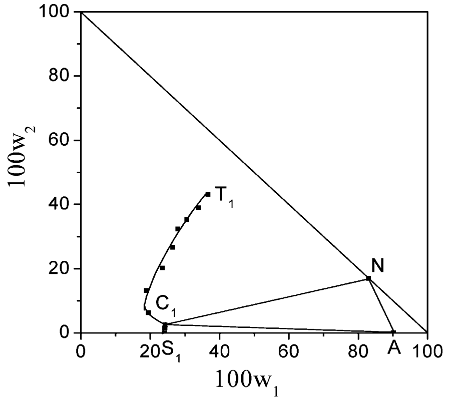

**Figure 2.** Equilibrium phase diagram of the ternary $K_2C_2O_4$ (1) + $H_2O_2$ (2) + $H_2O$ (3) system at 283.15 K: ■, experimental data point; —, experimental phase diagram; $S_1$, solubility of $K_2C_2O_4$ in water; $C_1$, co-saturated point; N, $K_2C_2O_4\cdot H_2O_2$; A, $K_2C_2O_4\cdot H_2O$; $T_1$, experimental data.

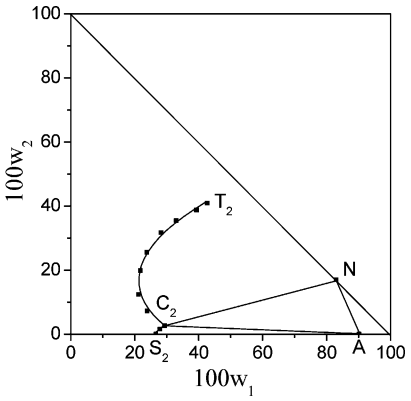

**Figure 3.** Equilibrium phase diagram of the ternary $K_2C_2O_4$ (1) + $H_2O_2$ (2) + $H_2O$ (3) system at 293.15 K: ■, experimental data point; —, experimental phase diagram; $S_2$, solubility of $K_2C_2O_4$ in water; $C_2$, co-saturated point; $T_2$, experimental data; N and A have the same meaning as described in Figure 1.

In Figures 2 and 3, along the solubility curve $C_1T_1$ or $C_2T_2$, linking the component points of liquid phase and moist solid phase and an extension thereof, the point of intersection of these tie-lines is approximately the solid-phase component for the compound ($K_2C_2O_4\cdot H_2O_2$) on a wet basis. Along the solubility curve $S_1C_1$ or $S_2C_2$, linking the component points of liquid phase and moist solid phase and an extension thereof, the point of intersection of these tie-lines is approximately the solid-phase component for $K_2C_2O_4\cdot H_2O$. The results indicated that two solids were present in the system: one was $K_2C_2O_4\cdot H_2O$, and the other was a double salt with the formula $K_2C_2O_4\cdot H_2O_2$. This result is in agreement with the graph and with direct analysis after drying of the compound obtained by crystallization at the given temperatures.

In the phase diagram as shown in Figures 2 and 3, there are three crystallization fields: $K_2C_2O_4\cdot H_2O_2$ ($T_1C_1N$ and $T_2C_2N$), $K_2C_2O_4\cdot H_2O$ ($S_1C_1A$ and $S_2C_2A$), mixture of $K_2C_2O_4\cdot H_2O_2$ and $K_2C_2O_4\cdot H_2O$ ($C_1NA$ and $C_2NA$) with $K_2C_2O_4\cdot H_2O$ having the smallest crystallization field. The double salt $K_2C_2O_4\cdot H_2O_2$ has a bigger crystallization field than either $K_2C_2O_4\cdot H_2O$ or the mixture. The large crystallization region in the phase diagram

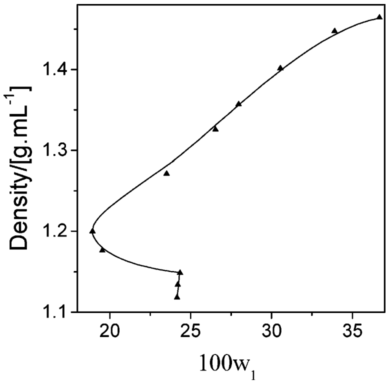

**Figure 4.** Density value−composition relationship diagram for the ternary $K_2C_2O_4$ (1) + $H_2O_2$ (2) + $H_2O$ (3) system at 283.15 K: ▲, experimental data point; −, experimental relationship diagram.

indicates that $K_2C_2O_4\cdot H_2O_2$ is of low solubility; therefore, most $K_2C_2O_4\cdot H_2O_2$ can crystallize from solution.

The phase diagram has two univariant curves. $C_1T_1$ and $C_2T_2$ are saturation curves corresponding to the solid-phase $K_2C_2O_4\cdot H_2O_2$ at (283.15 and 293.15) K, respectively. $S_1C_1$ and $S_2C_2$ are saturation curves corresponding to the solid-phase $K_2C_2O_4\cdot H_2O$. $C_1$ and $C_2$ are invariant points, which represent the equilibrium of the two solid phases $K_2C_2O_4\cdot H_2O$ and $K_2C_2O_4\cdot H_2O_2$.

Figures 2 and 3 further illustrate the temperature dependence of the phase diagram for the ternary $K_2C_2O_4$ + $H_2O_2$ + $H_2O$ system. When the temperature increases from (283.15 to 293.15) K, the solubility of $K_2C_2O_4\cdot H_2O$ and $K_2C_2O_4\cdot H_2O_2$ increases slightly, and the co-saturated point moves upward. The phase diagrams of the ternary system are similar at different temperatures. The crystalline region of the compound $K_2C_2O_4\cdot H_2O_2$ increases as the temperature decreases. It can also be seen from Figures 1 and 2 that the adduct $K_2C_2O_4\cdot H_2O_2$ is a symmetric double salt and can be formed at low concentrations of hydrogen peroxide.

On the basis of data collected in Tables 1 and 2, the relationship between the density of the equilibrium liquid phase and the salt concentration values expressed in mass fractions (Figures 4 and 5) were found. Results show that the equilibrium solution density values increased with respect to a rise in the hydrogen peroxide concentration.

## Conclusion

The solubility of the ternary potassium oxalate + hydrogen peroxide + water system at (283.15 and 293.15) K was determined experimentally. The (solid + liquid) phase diagram was constructed. The densities of the equilibrium liquid phase were obtained. The double salt $K_2C_2O_4\cdot H_2O_2$ was confirmed by Schreinemaker's wet residues method. At the studied temperatures, two solid phases were formed in the ternary $K_2C_2O_4$ + $H_2O_2$ + $H_2O$ system that correspond to $K_2C_2O_4\cdot H_2O$ and $K_2C_2O_4\cdot H_2O_2$. The phase diagram has three crystallization fields ($K_2C_2O_4\cdot H_2O_2$, $K_2C_2O_4\cdot H_2O$, and a mixture of $K_2C_2O_4\cdot H_2O_2$ and $K_2C_2O_4\cdot H_2O$), two univariant curves, and one invariant point at each temperature. The phase diagrams of the ternary system are similar at different temperatures. The double salt $K_2C_2O_4\cdot H_2O_2$ has a bigger crystallization field than that of the others. The solubilities of $K_2C_2O_4\cdot H_2O$ and $K_2C_2O_4\cdot H_2O_2$ increase slightly with increasing temperature, while the crystalline region of the compound $K_2C_2O_4\cdot H_2O_2$ decreases as the temperature increases.

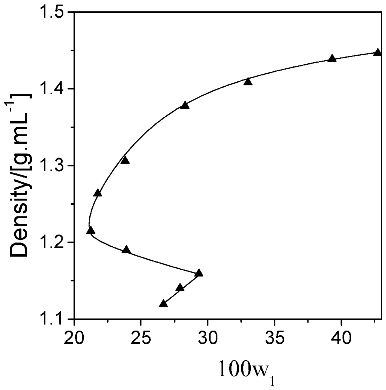

**Figure 5.** Density value−composition relationship diagram for the ternary system $K_2C_2O_4$ (1) + $H_2O_2$ (2) + $H_2O$ (3) at 293.15 K: ▲, experimental data point; −, experimental relationship diagram.

**Acknowledgment**

We appreciate the Editors and the anonymous reviewers for their valuable suggestions.

## Literature Cited

(1) Pederson, B. F.; Pederson, B. The crystal structure of potassium and rubidium oxalate monoperhydrate, $K_2C_2O_4\cdot H_2O_2$ and $Rb_2C_2O_4\cdot H_2O_2$. *Acta Chem. Scand.* **1967**, *21*, 779−790.
(2) Adams J. M.; Ramdas V.; Guarini G. G. T.; Adams C. J. Thermal decomposition of some alkali-metal oxalate monohydrates and monoperhydrates. *J. Chem. Soc. Dalton Trans.* **1980**, 269−275.
(3) Stephen, H.; Stephen, T. *Solubility of Inorganic and Organic Compounds;* Pergamon: Oxford, 1979.
(4) Zhao, H. K.; Ren, B. Z.; Liu, G. J. Phase diagram of the system urea + hydrogen peroxide + water. *J. Chem. Eng. Data* **2003**, *48*, 548−550.
(5) Pani, S.; Terrey, H. Compounds formed between hydrogen peroxide and sulphates, selenates, and tellurates in aqueous solution. *J. Chem. Soc.* **1955**, *155*, 3056−3063.
(6) Zhao, H. K.; Ren, B. Z.; Luo, T. L.; Li, J.; Liu, G. J. Phase diagram of the quaternary system sodium sulfate + sodium chloride + hydrogen peroxide + water and its subsystems: experimental data *J. Chem. Eng. Data* **2003**, *48*, 1540−1543.
(7) Nývlt, J. *Solid−Liquid Phase Equilibria*; Publishing House of Czechoslovak, 1977.

Received for review April 30, 2006. Accepted October 2, 2006. We thank the High Education Natural Science Foundation of Jiangsu Province (Grant HK051087) and the Open Project Program of the Key Laboratory of Physical Chemistry, Yangzhou University, China for their support.

JE060182Y