YU Xudong, ZENG Ying, YIN Qinghong, and PENG Yun, 2014. Thermodynamics Phase Equilibria for the Salt - Water System of Potassium and Rubidium Ions. *Acta Geologica Sinica* (English Edition), 88(supp. 1): 393-394.

# Thermodynamics Phase Equilibria for the Salt - Water System of Potassium and Rubidium Ions

YU Xudong[1], ZENG Ying[1, 2*], YIN Qinghong[1], and PENG Yun[1]

*1 College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610059, China*
*2 Mineral Resources Chemistry Key Laboratory of Sichuan Higher Education Institutions, Chengdu 610059, China*

## 1 Introduction

Brines, containing a variety of useful components, such as alkali metal (IA), alkaline earth metal (type IIA), halogen elements (such as VIIA), are naturally occurring complex electrolyte solution. Although rubidium is not the main component of the brine, while in the brine exploiting process, rubidium ion is continuously enriched in the mother liquid to form an aqueous system containing lithium, potassium, rubidium, magnesium, and chloride. In chloride solution, rubidium and potassium are easily formed into solid solution because of their similar ion radius: potassium, $1.33 \cdot 10^{-10}$ m, and rubidium, $1.49 \cdot 10^{-10}$ m. Besides that, the hydrated salts of $MgCl_2$ and double salts can be easily formed, which increase the difficulty to the comprehensive utilization of the brine.

The phase equilibria and phase diagram of aqueous systems of alkali halides are required not only in process design in the chemical industry, but they are of interest to a wider variety of geochemistry and salt chemistry. Up to now, some paper described phase equilibria aiming at rubidium and potassium coexist system have been reported. Kalinkin et al. have studied ternary system $K_2SO_4$ + $Rb_2SO_4$ + $H_2O$ at 298 K (Kalinkin and Rumyantsev, 1996), the system is of complex type with the continuous solid solutions between $K_2SO_4$ and $Rb_2SO_4$. Merbach et al. have studied the quaternary system KCl + RbCl + $H_2O$ at 298 K (Merbach and Gonella, 1969), results shown that there was only solid solution [(K, Rb)Cl] formed. The quaternary system KCl + RbCl + (CsCl) + $MgCl_2$ + $H_2O$ and its subsystems at 298 K have been done by J. D'Ans et al. (D'Ans and Brsch, 1937), results shown that there were single salts KCl, RbCl and solid solution [(K, Rb)Cl] formed in the KCl + RbCl + $H_2O$ system. In conclusion, the relevant phase relations of the rubidium and potassium coexist system are lacking, which affect the comprehensive utilization of rubidium and potassium in the brine.

To figure out the crystallization form and crystallization area of the solid solution of the potassium and rubidium coexist systems change with the temperature and coexist ions, the metastable phase equilibria of ternary system KCl + RbCl + $H_2O$ and quaternary system $Li^+$, $K^+$, $Rb^+$ // $Cl^-$ - $H_2O$ at (298, 323 and 348) K, and quaternary systems $K^+$, $Rb^+$, $Mg^{2+}$ // $Cl^-$ - $H_2O$ and $Li^+$, $Rb^+$, $Mg^{2+}$ // $Cl^-$ - $H_2O$ at 323 K have been done by our research group.

## 2 Results and Discussion

Figure 1 is the metastable phase diagrams of ternary system KCl + RbCl + $H_2O$ at (298, 323 and 348) K (Yu et al., 2010, 2011, 2013). The solid solution [(K, Rb)Cl] was formed and the crystallization region of the solid solution almost occupies all the phase region. The crystallization zones of the single salts enlarged along with the increase in the temperature, whereas the crystallization zone of

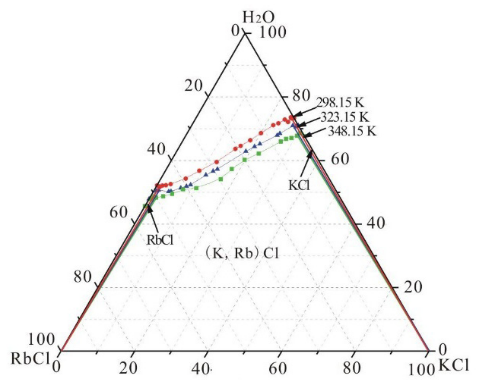


Fig. 1. Metastable phase diagram of ternary system KCl + RbCl + $H_2O$ at (298, 323 and 348) K.

* Corresponding author. E-mail: xwdlyxd@gmail.com

solid solution decreased. Results show that the increment of temperature is conducive to separate potassium chloride from the chloride solution. Comparisons between the metastable and stable phase diagrams (Merbach and Gonella, 1969) at 298 K show that besides solid solution [(K, Rb)Cl], the single salts KCl and RbCl are simultaneously formed.

Figure 2 is the metastable phase diagrams of quaternary system $Li^+$, $K^+$, $Rb^+$ // $Cl^-$ - $H_2O$ at 298 K ~ 348 K (Yu et al., 2012; Li et al., 2013; Yin et al., 2013). The crystallization region of salts in the quaternary system decrease in the order of [(K, Rb)Cl], KCl, $LiCl{\cdot}H_2O$, and RbCl. The crystallization zones of the single salts enlarged along with the increase in the temperature, whereas the crystallization zone of solid solution decreased.

Figure 3 is the metastable phase diagram of quaternary system $K^+$, $Rb^+$, $Mg^{2+}$ // $Cl^-$ - $H_2O$ at 323 K (Jiang et al., 2013). There are two carnallite type double salts $RbCl{\cdot}MgCl_2{\cdot}6H_2O$, $KCl{\cdot}MgCl_2{\cdot}6H_2O$ and a solid solution [(K, Rb)Cl] formed in the system. The solid solution has the largest crystallization field almost occupies the entire phase region, the salt $MgCl_2{\cdot}6H_2O$ has the smallest crystallization field.

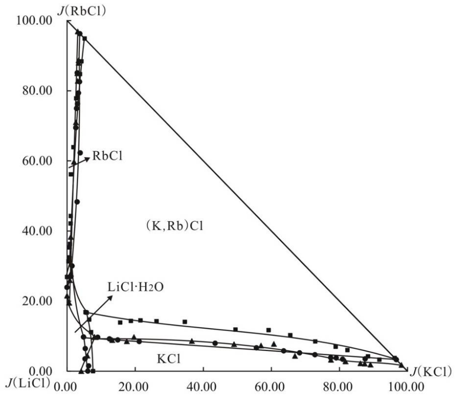


Fig. 2. Metastable phase diagram of quaternary system $Li^+$, $K^+$, $Rb^+$ // $Cl^-$ - $H_2O$ at (298, 323 and 348) K(▲ 298 K、● 323 K、■ 348 K).

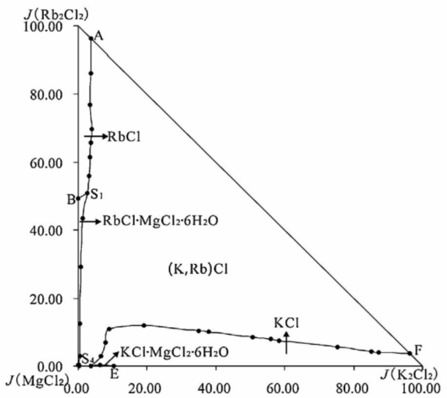


Fig. 3. Metastable phase diagram of quaternary system $K^+$, $Rb^+$, $Mg^{2+}$ // $Cl^-$ - $H_2O$ at 323 K.

**Key words**: phase equilibria, potassium, rubidium, solid solution.

## Acknowledgements

Project supported by National High Technology Research and Development Program of China (2012AA061704), China National Nature Science Foundation (No. 41173071), the Research Fund for the Doctoral Program of Higher Education from the Ministry of Education of China (20115122110001), the Sichuan Youth Science and Technology Innovation Research Team Funding Scheme (2013TD0005), and Innovation Team of CDUT(KYTD201405).

**References**

D'Ans, J., and Brsch, F, 1937. Über die Fraktionierung inkongruent löslicher isomorpher Doppelsalze Die quaternären Systeme KCl-RbCl-(CsCl)-$MgCl_2$-$H_2O$ bei 25 ℃. *Zeitschrift für anorganische Chemie,* 232(4): 337–368.

Jiang Dongbo, Zeng Ying and Yu Xudong, 2013. Metastable phase equilibria for the quaternary system containing potassium, magnesium, rubidium and chloride at 323.15 K. *Fluid Phase Equilibria,* 349: 67–70.

Kalinkin, A. M., and Rumyantsev, A. V, 1996. Thermodynamics of phase equilibria of the $K_2SO_4$ + $Rb_2SO_4$ + $H_2O$ system at 25 ℃. *J. Solution Chem,* 25(7): 695–709.

Li Zhongquan, Yu Xudong, Yin Qinghong and Zeng Ying, 2013. Thermodynamics metastable phase equilibria of aqueous quaternary system LiCl + KCl + RbCl + $H_2O$ at 323.15 K. *Fluid Phase Equilibria,* 358: 131–136.

Merbach, A., and Gonella, J., 1969. Contribution à l'étude du système quaternaire KCl-RbCl-CsCl-$H_2O$: I. Les isothermes de 25° des système ternaires limites. *Helv. Chim. Acta,* 52(1): 69–76.

Yu Xudong and Zeng Ying, 2010. Metastable phase equilibria in the aqueous ternary systems KCl + $MgCl_2$ + $H_2O$ and KCl + RbCl + $H_2O$ at 323.15 K. *J. Chem. Eng. Data,* 55(12): 5771–5776.

Yu Xudong, Zeng Ying, Yao Huixin and Yang Jianyuan, 2011. Metastable Phase Equilibria in the Aqueous Ternary Systems KCl + $MgCl_2$ + $H_2O$ and KCl + RbCl + $H_2O$ at 298.15 K. *J. Chem. Eng. Data,* 56(8): 3384–3391.

Yu Xudong, Zeng Ying and Yang Jianyuan, 2012. Solid - liquid isothermal evaporation metastable phase equilibria in the aqueous quaternary system LiCl + KCl + RbCl + $H_2O$ at 298.15 K. *J. Chem. Eng. Data,* 57(1):127–132.

Yu Xudong, Zeng Ying, Yin Qinghong and Mu Pengtao, 2012. The solubilities, densities, and refractive indices of the ternary systems KCl + RbCl + $H_2O$ and KCl + $MgCl_2$ + $H_2O$ at 348.15 K. *J. Chem. Eng. Data,* 57(12): 3658–3663.

Yin Qinghong, Zeng Ying, Yu Xudong, Mu Pengtao and Tan Qi, 2013. Metastable phase equilibrium in the quaternary system LiCl + KCl + RbCl + $H_2O$ at 348.15 K. *J. Chem. Eng. Data,* 58(10): 2875–2880.