

CHEMICAL THERMODYNAMICS  
AND THERMOCHEMISTRY

Solid-Liquid Phase Equilibria in the Quaternary System  
(NaCl–KCl–SrCl<sub>2</sub>–H<sub>2</sub>O) at 288.15 K

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**Abstract**—Phase equilibria of the quaternary system (NaCl–KCl–SrCl<sub>2</sub>–H<sub>2</sub>O) at 288 K are studied by the isothermal dissolution equilibrium method. The liquid phase was subjected to chemical analysis, and the corresponding solid phase was identified via X-ray diffraction. The phase diagram was plotted according to the experimental data. In the system of (NaCl–KCl–SrCl<sub>2</sub>–H<sub>2</sub>O), there are one invariant point, three univariant curves and three crystallization regions. The invariant point corresponding to NaCl + KCl + SrCl<sub>2</sub> · 6H<sub>2</sub>O + Liquid, three crystallization regions corresponding to the NaCl, KCl, SrCl<sub>2</sub> · 6H<sub>2</sub>O. Double salt or solid solution was not formed between the three original components NaCl, KCl and SrCl<sub>2</sub> · 6H<sub>2</sub>O that without dehydration. The crystallization field of KCl is the largest, it is also found that strontium chloride has the salting-out effect on NaCl and KCl in this quaternary system.

**Keywords:** phase equilibria, phase diagram, solubility, strontium chloride

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INTRODUCTION

Liquid mineral resources are an important type of natural resources. China's inorganic salt liquid deposit resources mainly include seawater, well brine, salt lake brine and oil field brine. The brine water resources in the salt lakes have been developed and utilized in large quantities. Oilfield brine refers to the high salinity brine that occurs in the oil and gas fields. These brines may contain trace elements, especially Br, I, B, NH<sub>3</sub>, Li, Rb, Cs, Sr, and other elements with high ion content. With the acceleration of the development of oil and gas fields and the rapid expansion of production scale, the water production of oilfields has increased sharply, and the era of large-scale development and utilization of oilfield brine water resources has arrived.

Located in the Nanyishan region in the west of the Qaidam basin, the oil and gas exploration is often accompanied by the eruption of highly mineralized brine (oilfield water), which is rich in potassium, boron, strontium, lithium and other resources. After treatment, the oilfield water in this region can be approximately summarized as complex system of Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>//Cl<sup>-</sup>–H<sub>2</sub>O [1]. According to the investigation and evaluation of geological survey institute of Qinghai province, the reserves of valuable components are huge, which the reserves of potassium

chloride are about 250 million tons, the reserves of strontium chloride are about 25.12 million tons, and the reserves of lithium chloride are about 224.8 million tons [2]. The application of strontium involves electronic, chemical, ceramic, metallurgy, glass and other industrial fields.

Many scholars have carried out research on the strontium-containing water salt system. For example, in the 1950s, Assarsson [3–6] conducted a series of studies on the phase equilibrium of the strontium-containing water salt system. It was found that calcium strontium chloride solid solution was formed when the system contains strontium chloride and calcium chloride. Li [7] and Sun [8, 9] studied the phase diagram of ternary systems (NaCl–SrCl<sub>2</sub>–H<sub>2</sub>O) and (KCl–SrCl<sub>2</sub>–H<sub>2</sub>O) at 298 and 348 K. At 298 K, strontium chloride contains six molecules of crystallization water, while at 348 K, strontium chloride contains two molecules of crystallization water. The phase equilibrium of (CaCl<sub>2</sub>–SrCl<sub>2</sub>–H<sub>2</sub>O) at 298 K found that solid solution formed in the system, namely calcium salt as solid solution and strontium salt as solid solution. In addition, the system (NaBr–MgBr<sub>2</sub>–SrBr<sub>2</sub>–H<sub>2</sub>O) and (KBr–MgBr<sub>2</sub>–SrBr<sub>2</sub>–H<sub>2</sub>O) at 323 K [10], and the system (NaBr–KBr–SrBr<sub>2</sub>–H<sub>2</sub>O) at 348 K [11] have been reported previously, but the solubility data and the corresponding equilibrium solid phases for

**Table 1.** Chemicals used in this study

Chemicals	Final mass fraction purity	Analysis method
NaCl	0.995	ICP-OES for Na <sup>+</sup>
KCl	0.995	Gravimetric method for K <sup>+</sup>
SrCl <sub>2</sub> · 6H <sub>2</sub> O	0.992	Titration method for Sr <sup>2+</sup>

the system containing strontium are still not sufficient. The average temperature of the Nanyishan region in summer is about 288.15 K, so the phase equilibria study of system (NaCl–KCl–SrCl<sub>2</sub>–H<sub>2</sub>O) at 288.15 K will be of great value for separating and purifying the strontium salts from the brines. In this paper, the phase equilibria for the quaternary system (NaCl–KCl–SrCl<sub>2</sub>–H<sub>2</sub>O) at 288.15 K were presented by the isothermal dissolution equilibrium method.

## EXPERIMENTAL

**Apparatus and reagents.** The chemicals used in this study were shown in Table 1. All reagents were purchased from Sinopharm Chemical Reagent Co. Ltd, and were purified by recrystallization. The thermostatic bath with magnetic stirring (Beijing Hui Cheng Jia Instrument Technology Co. Ltd) was used to control the temperature with a precision of 0.01 K. An atomic absorption spectrophotometer (AA320, Shanghai Precision Scientific Instruments Co. Ltd) was employed to determine the concentrations of Na<sup>+</sup> in solution.

**Experimental methods.** The isothermal dissolution method was used in this study. This method requires to take the quantity of the salt needed for saturation of the primary system according to the data in the literature, and then adding another salt, from zero to the excess. Each univariate curve is prepared in a certain ratio with 6–10 samples, the samples in the experiment were placed in a glass bottle, and then deionized water was added to each sample, sealed with a rubber stopper, and placed in a constant temperature water bath stirring tank at (288.15 ± 0.01 K). The supernatant was sampled every other day for analysis, and the system reached equilibrium when the liquid phase composition of the solution was constant. After the solution reaches equilibrium, the stirring is turned off, and the mixture is allowed to stand for a while at the constant temperature stirring tank. When the upper liquid is clarified, an appropriate amount of the solution is taken into the weighing bottle for weighing, and the mass of the taken solution is obtained by subtraction. The composition of the equilibrium liquid phase is determined by chemical analysis and instrumental

methods. The equilibrium solid phase of some systems was identified by X-ray diffraction.

**Analytical methods.** The K<sup>+</sup> ion concentration was determined by the gravimetric method with sodium tetraphenylborate, and the relative error of the analytical results is less than ±0.003 in mass fraction. The Cl<sup>–</sup> ion concentration was determined by AgNO<sub>3</sub> titration in the presence of K<sub>2</sub>CrO<sub>4</sub> as indicator, and the resulting uncertainty was within ±0.003 in mass fraction [12]. The Sr<sup>2+</sup> ion concentration was analyzed by titration with EDTA standard solution, and the resulting uncertainty was within ±0.005 in mass fraction [9]. The Na<sup>+</sup> ion concentration was evaluated according to ion balance.

## RESULTS AND DISCUSSION

The solubility of SrCl<sub>2</sub> in the binary system (SrCl<sub>2</sub> + H<sub>2</sub>O) from 273.15 to 373.15 K has been reported [3, 7, 9, 13, 14]. It was observed that the solubility of SrCl<sub>2</sub> increases with the increasing of temperature. The solubilities of SrCl<sub>2</sub> in water at 288.15 K obtained in this work and from literature [13] are 33.68 and 33.7 in mass percentage, and the deviations is 0.06%. The results show that the experimental results in this work agree well with the literature data, demonstrating that our experimental procedure and analysis are reliable.

**Phase diagram of the quaternary system (NaCl–KCl–SrCl<sub>2</sub>–H<sub>2</sub>O).** The investigation of the phase equilibria of the quaternary system (NaCl–KCl–SrCl<sub>2</sub>–H<sub>2</sub>O) was carried out in accordance with the experimental method of isothermal dissolution. The solubility of each component in the equilibrium solution was measured. The equilibrium solubility test results are shown in Table 2. The solubility of the equilibrium liquid phase is expressed by mass percentage. On the basis of  $J(\text{SrCl}_2) + J(\text{KCl}) + J(\text{NaCl}) = 100$  g, the calculation formula is as follows (1)–(4), the dry basis diagram of the quaternary system (KCl–NaCl–SrCl<sub>2</sub>–H<sub>2</sub>O) at 288.15 K can be obtained, and is shown in Fig. 1. The compositions are expressed in dry-basis index, where  $J(\text{NaCl})$ ,  $J(\text{KCl})$ ,  $J(\text{SrCl}_2)$ , and  $J(\text{H}_2\text{O})$  are defined as following:

$$J(\text{NaCl}) = \frac{w(\text{NaCl})}{w(\text{NaCl}) + w(\text{KCl}) + w(\text{SrCl}_2)} \times 100, \quad (1)$$

$$J(\text{KCl}) = \frac{w(\text{KCl})}{w(\text{NaCl}) + w(\text{KCl}) + w(\text{SrCl}_2)} \times 100, \quad (2)$$

**Table 2.** Solubilities in the quaternary system (NaCl + KCl + SrCl<sub>2</sub> + H<sub>2</sub>O) at 288.15 K

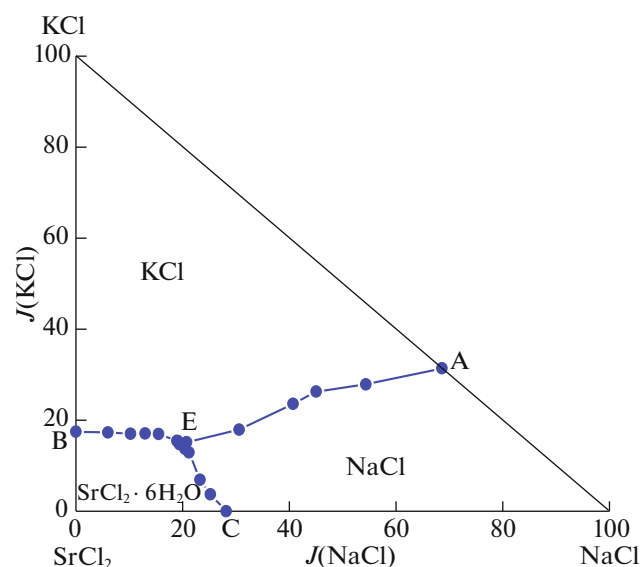
No.	Composition of liquid phase, $w_b \times 10^2$			Jänecke index (g/100 g of salt)				Solid phase
	NaCl	KCl	SrCl <sub>2</sub>	NaCl	KCl	SrCl <sub>2</sub>	H <sub>2</sub> O	
1	0.00	0.00	33.68	0.00	0.00	100	196.91	SrCl <sub>2</sub> · 6H <sub>2</sub> O
2, A	21.10	9.65	0.00	68.62	31.38	0.00	225.20	NaCl + KCl
3	17.56	9.01	5.74	54.35	27.89	17.77	209.50	NaCl + KCl
4	15.16	8.86	9.65	45.03	26.31	28.66	197.00	NaCl + KCl
5	14.10	8.18	12.35	40.72	23.62	35.66	188.77	NaCl + KCl
6	11.05	6.48	18.60	30.58	17.94	51.48	176.78	NaCl + KCl
7	7.90	5.79	24.42	20.73	15.19	64.08	162.40	NaCl + KCl
8	7.52	5.71	25.51	19.41	14.74	65.85	158.13	NaCl + KCl
9, B	0.00	6.33	29.92	0.00	17.46	82.54	175.86	KCl + SrCl <sub>2</sub> · 6H <sub>2</sub> O
10	2.20	6.35	28.13	6.00	17.31	76.69	172.63	KCl + SrCl <sub>2</sub> · 6H <sub>2</sub> O
11	3.86	6.41	27.36	10.26	17.03	72.71	165.75	KCl + SrCl <sub>2</sub> · 6H <sub>2</sub> O
12	4.91	6.48	26.51	12.96	17.10	69.95	163.85	KCl + SrCl <sub>2</sub> · 6H <sub>2</sub> O
13	5.94	6.50	25.94	15.48	16.94	67.59	160.55	KCl + SrCl <sub>2</sub> · 6H <sub>2</sub> O
14	7.37	5.94	25.26	19.11	15.40	65.49	159.27	KCl + SrCl <sub>2</sub> · 6H <sub>2</sub> O
15, E	7.35	5.99	25.46	18.94	15.44	65.62	157.73	NaCl + KCl + SrCl <sub>2</sub> · 6H <sub>2</sub> O
16	7.86	5.28	25.34	20.43	13.72	65.85	159.88	NaCl + SrCl <sub>2</sub> · 6H <sub>2</sub> O
17	7.85	4.79	24.40	21.19	12.93	65.87	169.98	NaCl + SrCl <sub>2</sub> · 6H <sub>2</sub> O
18	8.36	2.48	25.08	23.27	6.90	69.82	178.40	NaCl + SrCl <sub>2</sub> · 6H <sub>2</sub> O
19	8.98	1.33	25.34	25.19	3.73	71.08	180.50	NaCl + SrCl <sub>2</sub> · 6H <sub>2</sub> O
20, C	9.96	0.00	25.39	28.18	0.00	71.82	182.89	NaCl + SrCl <sub>2</sub> · 6H <sub>2</sub> O

$$J(\text{SrCl}_2) = \frac{w(\text{SrCl}_2)}{w(\text{NaCl}) + w(\text{KCl}) + w(\text{SrCl}_2)} \times 100, \quad (3)$$

$$J(\text{H}_2\text{O}) = \frac{w(\text{H}_2\text{O})}{w(\text{NaCl}) + w(\text{KCl}) + w(\text{SrCl}_2)} \times 100. \quad (4)$$

In Fig. 1, there are one invariant point, three univariant curves and three crystallization regions in the quaternary system (KCl–NaCl–SrCl<sub>2</sub>–H<sub>2</sub>O) at 288.15 K. The invariant point corresponding to (NaCl + KCl + SrCl<sub>2</sub> · 6H<sub>2</sub>O + Liquid), and the compositions of NaCl, KCl, and SrCl<sub>2</sub> in the liquid phase with mass fraction ( $10^2w$ ) are 7.35, 5.99, and 25.46, respectively; three univariant isothermal dissolution curves of AE, BE, and CE, indicating the cosaturation of two salts; three crystallization regions corresponding to the NaCl + Liquid, KCl + Liquid, SrCl<sub>2</sub> · 6H<sub>2</sub>O + Liquid. Among them, the largest crystallized area is KCl, and the smallest is SrCl<sub>2</sub> · 6H<sub>2</sub>O. Due to the high solubilities of strontium chloride, there is a strong salting-out effect to KCl. Double salt or solid solution was not formed between the three original components NaCl, KCl, and SrCl<sub>2</sub> · 6H<sub>2</sub>O that without dehydration.

Figure 2 is the water-phase diagram of the quaternary system at 288.15 K, and it shows that the Jänecke index values of  $J(\text{H}_2\text{O})$  gradually change with increasing  $J(\text{NaCl})$ .

**Fig. 1.** Dry-salt phase diagram of the quaternary system (NaCl + KCl + SrCl<sub>2</sub> + H<sub>2</sub>O) at 288.15 K.

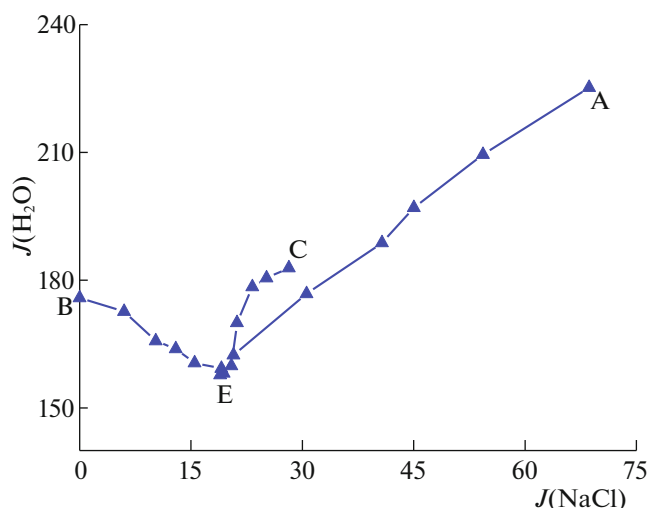


Fig. 2. Water-phase diagram of the quaternary system (NaCl + KCl + SrCl<sub>2</sub> + H<sub>2</sub>O) at 288.15 K.

In order to further confirm the solid phase, the X-ray diffraction analysis was used which can be used for qualitative analysis and identification of solid phase, then compare the measured lattice plane spacing and diffraction intensity with diffraction data of the solid standard phase, which can determine the phase in the solid phase. Figure 3 shows the X-ray diffraction patterns of invariant point. The abscissa is the  $2\theta$  from  $5^\circ$  to  $90^\circ$ ; the vertical ordinate is the intensity. The X-ray diffraction pattern of the invariant point was well matched to standard diffraction pattern of NaCl, KCl, and SrCl<sub>2</sub> · 6H<sub>2</sub>O with powder diffraction file (pdf) nos. 05-0628, 41-1476, 06-0073, respec-

tively. It shows that salts NaCl, KCl, and SrCl<sub>2</sub> · 6H<sub>2</sub>O coexist at the invariant point.

The comparison of the solubility data for the quaternary system (NaCl–KCl–SrCl<sub>2</sub>–H<sub>2</sub>O) at 323.15 K [15] and 288.15 K (this study) is shown in Fig. 4. It was found that the solid phase numbers and the patterns for the solubility curves at different temperatures are similar; while the area of crystallization region of KCl and SrCl<sub>2</sub> · 6H<sub>2</sub>O decreased obviously as the temperature increases from 288.15 to 343.15 K while that of NaCl increased with the increasing temperature. These changes indicate that the solubility of potassium chloride and strontium chloride is positively correlated with temperature, which implies that it is suitable to use the temperature variation effects to separate the strontium chloride salts.

## CONCLUSIONS

The isothermal dissolution equilibrium method was employed to investigate the solid-liquid equilibria of quaternary system (NaCl–KCl–SrCl<sub>2</sub>–H<sub>2</sub>O) at 288.15 K, which determined invariant point and crystallization regions. According to experimental data, the phase diagrams was plotted. Phase diagram of the quaternary system consist of one invariant point (NaCl + KCl + SrCl<sub>2</sub> · 6H<sub>2</sub>O + Liquid) and three crystallization regions corresponding to NaCl, KCl, and SrCl<sub>2</sub> · 6H<sub>2</sub>O. When the experimental phase diagram at 288.15 K was compared with that at 343.15 K,

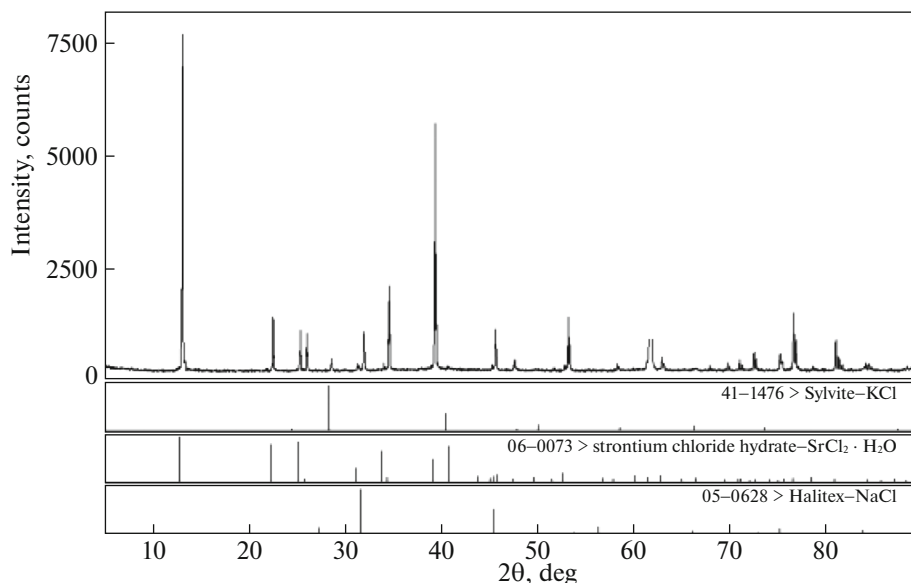
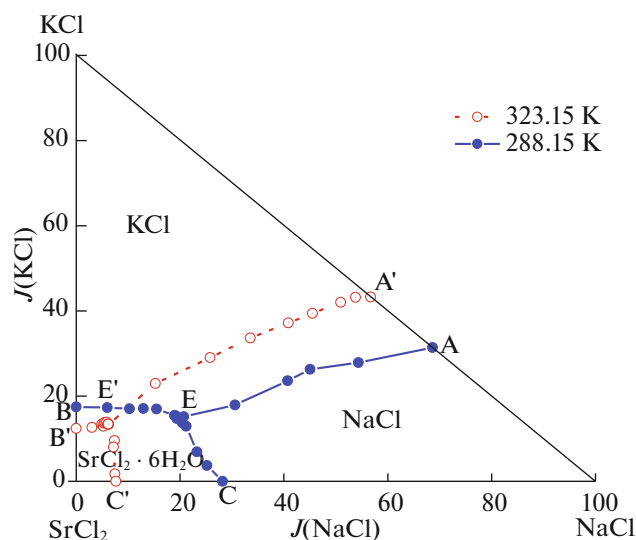


Fig. 3. X-ray diffraction pattern of the invariant point E (NaCl + KCl + SrCl<sub>2</sub> · 6H<sub>2</sub>O).



**Fig. 4.** (Color online) Comparison of phase diagram of the quaternary system (NaCl + KCl + SrCl<sub>2</sub> + H<sub>2</sub>O) at 288.15 and 323.15 K. —●—, Isothermal dissolution curve at 288.15 K (this work); ..○.., isothermal dissolution curve at 323.15 K.

it shows that the area of crystallization region of NaCl is increased with the increasing of temperature, while that of KCl and SrCl<sub>2</sub> · 6H<sub>2</sub>O is decrease obviously.

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