

A new method of determining solubility of salts and simple salt mixtures at higher temperatures (0 to 200°C) and up to 100 bars pressure

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MS received 13 October 1986; revised 13 July 1987

Abstract. A new apparatus has been designed and fabricated to determine the solubility of salts and simple salt mixtures at higher temperatures and pressures. The apparatus can be used to determine the solubility of salts at temperatures from 0 to 200°C and pressures upto 100 bars. The apparatus has been tested by determining the solubility of NaCl at temperatures from 30 to 200°C, while that of KCl was determined from 30 to 200°C. The phase equilibrium of the ternary system NaCl–KCl–H₂O has been established at two different temperatures 129.2°C and 159.2°C and under pressures upto 50 bars; extrapolations were upto 200°C.

Keywords. Solubility; hydrothermal fluids; brines; power plant; invariant point.

1. Introduction

Knowledge about the solubilities of salts in water is important in understanding the existence and nature of these salts occurring in the earth as minerals or as hydrothermal fluids, to understand sub-oceanic hydrothermal springs and also to have an idea about the separation of such salts from a mixture of them. Such knowledge about the solubilities of salts at their saturation equilibrium also throws light on the thermodynamic stability of salt deposits (Marshall 1985) on the disposal of radioactive wastes in ocean (Ctyne *et al* 1981), and on the scale formations of salts in boiler feed water and in power plants (Tomlinson 1985).

A large amount of experimental data is available in the literature on the solubility of several salts at higher and normal temperatures and normal pressures. The solubilities of salts at higher temperatures as well as higher pressures are also of equal importance as for instance the pressure inside the earth varies from one bar to about thousands of bars and temperature varies from the normal to a few thousands of degrees. However, very few such data are available in the literature, particularly for mixtures.

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The solubilities of salts at higher temperatures, approximately 400°C, is usually determined by three different methods, namely, quenching methods, visual observation and indirect methods (Marshall 1985; Cytne *et al* 1981; Booth and Bidwell 1950; Valyashko 1973). However, all these methods have their own drawbacks (Marshall 1985; Valyashko 1973).

Therefore in the present study we have designed and constructed a new apparatus using which the solubilities of salts at higher temperatures (upto 200°C) and at pressures (upto 100 bars) can be determined. The same apparatus can also be used to study the solubilities of simple ternary systems like NaCl–KCl–H₂O in which no double-salt formation occurs.

2. Apparatus

The autoclave along with the sample collector unit is shown in figure 1a. The autoclave Z, made of stainless steel (1880 CrNi), and is of 90 mm length, its inside and outside diameters are 40 mm and 50 mm respectively. The inside of the cell is lined with Ti metal (2 mm in thickness) so as to reduce the corrosion of the cell due to highly concentrated salt solutions.

The lid of the cell is a temperature-resistant stainless steel flange (material ATS 340). To minimize pressure leakages a teflon ring is used together with two delta rings between the cell and the lid as shown in figure 1b. In order to take out samples for analysis from the system the lid is provided with a capillary K of 67.5 mm length and 3 mm inner diameter. One end of the capillary which is inside the solution is equipped with three small meshes one on another, each of which is less than 0.1 mm. With the help of a spindel press SP (figure 1a) samples are drawn from the system without altering the equilibrium conditions. The lid is also provided with a stirrer R of length 79 mm and diameter 17 mm as shown in figure 1b. Furthermore, the lid consists of a pressure transducer part P, which in turn is connected to a millivoltmeter (standardised against the Bourdon pressure gauge).

The temperature of the experimental solution is measured with the help of a chromel-alumel thermoelement T₃ immersed in the solution. Two more such thermoelements T₁ and T₂ are used to record the temperatures of the bottom and middle parts of the autoclave. The temperatures at the valves, capillaries, and spindel press are controlled by similar thermoelements T₄, T₅ and T₆ respectively. The sample collector PG is made of titanium and has a volume of 13 cm³.

Initially N₂ gas at 15 bars pressure is applied through valves V₃ and V₄. The autoclave is placed in an aluminium jacket A1 which is heated by a heating coil H₁. The valves and capillaries are heated by H₂ and another heating coil H₃ is used to heat the spindel press.

3. Experiments

For binary systems experiments were carried out by taking a saturated solution (at room temperature) of the respective salt and N₂ then adding excess of the salt into the solution in the autoclave. The autoclave was closed and N₂ gas at 15 bars pressure initially applied. The system was continuously stirred while heating slowly to the

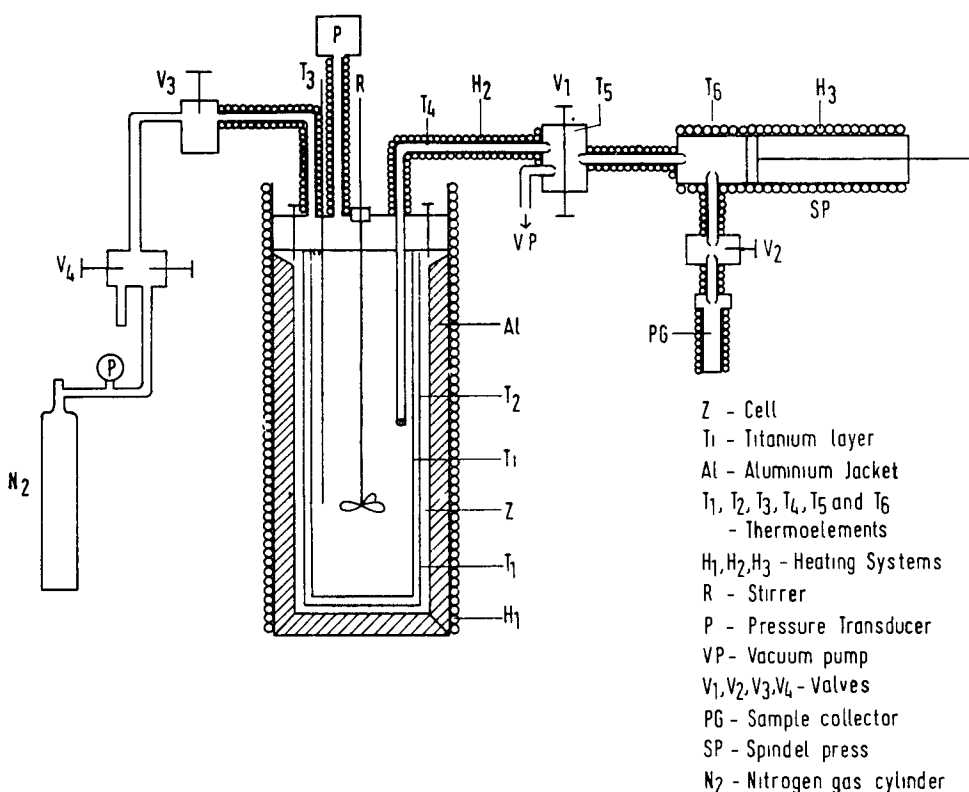


Figure 1a. Apparatus for determining the solubility of aqueous salt systems at higher temperatures and pressures.

desired temperature. The system was maintained at the required temperature ($\pm 0.2^\circ\text{C}$) for about 3 to 4 hours to attain equilibrium. Before taking out the sample the stirring of the solution was stopped and the pressure was noted. The sample was drawn into the collector using the spindel press without disturbing the equilibrium of the system. The sample was cooled along with the system, weighed and analysed for its composition. Merck extra-pure grade KCl and Merck GR grade NaCl were used without further purifications. N₂ gas 99.99% purity, supplied by Griesheim, was used. Chloride was estimated by titration and potassium by atomic absorption spectroscopy. All experiments were repeated till reproducible results were obtained. For ternary systems the experiments were carried out in a similar fashion by adding small amounts of the second salt. This was continued till the invariant point was reached, where both the salts are in equilibrium with their saturated solution. The point was checked by starting the experiments from both A and B points.

4. Results and discussion

4.1 Binary system

Experiments were carried out to determine the solubilities of individual salts NaCl and KCl at temperatures 30°C to 200°C under pressure. The data (± 0.05) are given

Table 1. Solubility of NaCl in water at 16 bars.

Temperature (°C)	Concentration of solution, g % (by weight)
30.0	26.42
75.6	26.72
100.4	27.98
123.1	28.17
149.5	29.62
200.0	34.19

Table 2. Solubility of KCl in water at 16 bars.

Temperature (°C)	Concentration of solution, (g % by weight.)
30.0	26.32
75.2	33.45
100.5	36.21
112.5	37.66
123.7	38.31
145.2	39.42
153.4	39.69
168.5	41.91
195.2	44.08

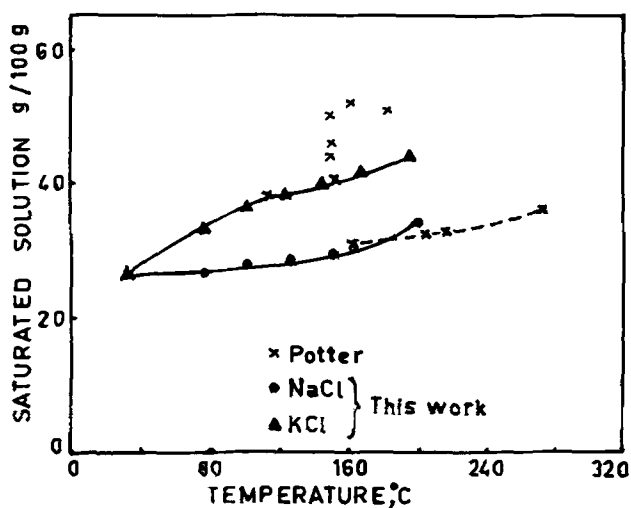
**Figure 2.** Temperature effect on the solubility of NaCl-H₂O and KCl-H₂O (Clyne *et al* 1981).

Table 3. Solubility data in ternary system NaCl-KCl-H₂O.

Temperature, °C	Point	Concentration of the solution*		Solid phase	
		NaCl	KCl		
25°C	A	26.48	0.0	NaCl	
		24.58	3.34	NaCl	
		22.11	8.16	NaCl	
	I	20.42	11.14	NaCl + KCl	
		13.45	15.71	KCl	
		12.32	16.58	KCl	
	B	—	26.52	KCl	
	129.2°C	A	29.50	—	NaCl
			28.72	3.59	NaCl
27.74			6.84	NaCl	
25.16			7.52	NaCl	
23.59			9.52	NaCl	
22.16			13.87	NaCl	
I		17.70	25.57	NaCl + KCl	
		12.32	26.08	KCl	
		13.49	28.88	KCl	
		6.34	32.51	KCl	
		0.76	37.21	KCl	
		B	—	38.61	KCl
159.2°C		A	31.18	—	NaCl
			27.16	6.52	NaCl
			27.63	11.50	NaCl
	25.84		10.29	NaCl	
	19.74		20.93	NaCl	
	22.05		22.11	NaCl	
	I	16.07	29.49	NaCl + KCl	
		15.87	26.62	KCl	
		10.21	32.31	KCl	
		4.72	36.62	KCl	
		B	—	40.37	KCl

*In g/100 g saturated solution 25°C data is from Siedel and Linke (1965).

with data for 25°C from the literature (Siedel and Linke 1965). These data are plotted in figures 3 and 4 as triangular and prismatic projections respectively showing the extrapolation of the ternary system from 159.2°C to 200°C by dashed lines. One can see from figure 3 that the solubilities of individual salts increase as the temperature increases. The increase in solubility of KCl is much more pronounced than that of NaCl, in accordance with the observations made using binary systems. The effect of temperature is more pronounced on the solubility of KCl and particularly on the invariant point I, as seen from figures 3 and 4. The curves AI and IB show the boundary surfaces between the solid salt and solutions. One can clearly see the effect of temperature on the fields occupied by individual salts NaCl and KCl and the shift in the invariant point in the triangular and prismatic projections of the system. The present method is useful only for simple salts and salt mixtures (with no double-salt formation).

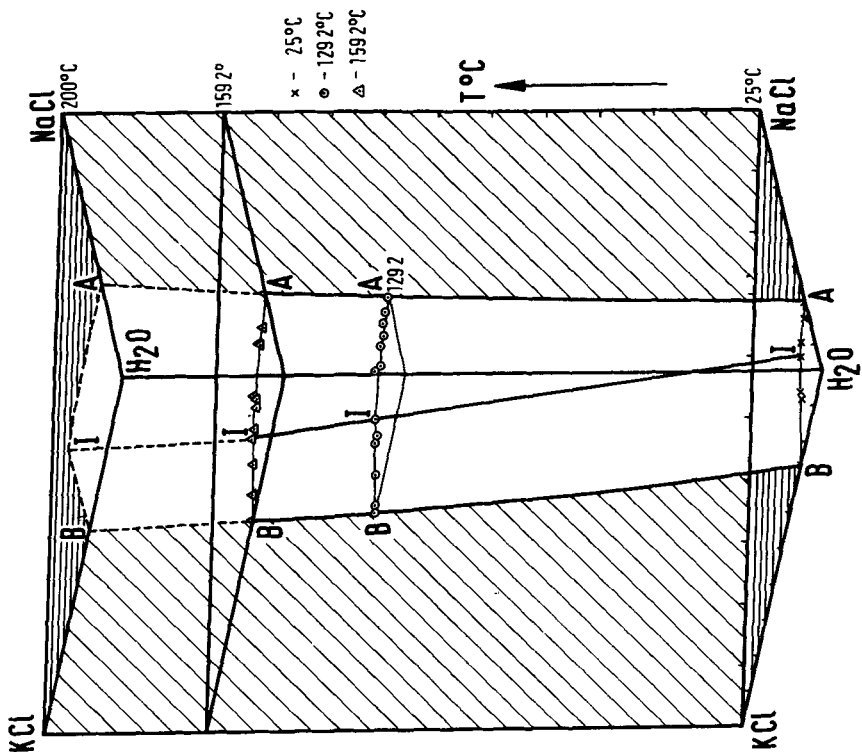


Figure 4. Prismatic projections of NaCl-KCl-H₂O showing the isotherms at 25, 129.2 and 159.2°C.

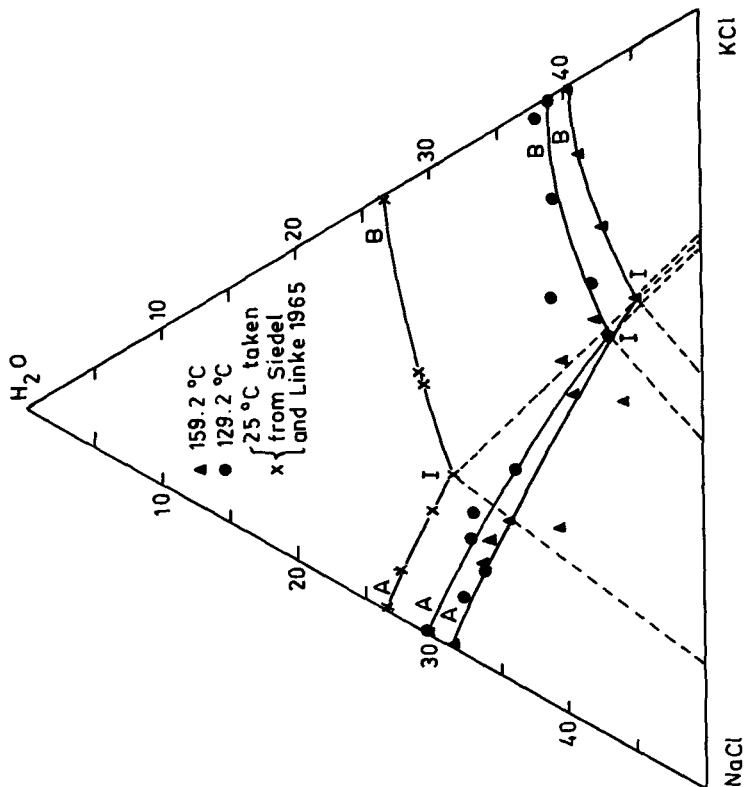


Figure 3. Solubility isotherms in the system NaCl-KCl-H₂O.

Acknowledgements

One of the authors, V R K S Susarla, thanks DAAD for the fellowship and also the Petrographic Department, University of Karlsruhe, for permission to carry out atomic absorption measurements.

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