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Conductivity of NaCl solution at 0.4—5.0 GPa and 25—500 ℃*

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Abstract NaCl-H_2O is the most fundamental ternary system in geology. Until now, the measurements of electrical conductivity of NaCl solutions are still little at high pressures (>0.5 GPa). We measured the conductivity of 0.01 m NaCl solution at 0.4—5.0 GPa and 25—500℃. The results are consistent with that of Quist and Marshall (1968) at 0.4 GPa. The conductivity of NaCl solution increases with increasing temperature. The results also show that the conductivity of NaCl solution changes little with increasing pressure below 1.5 GPa and changes rapidly with increasing pressure above 1.5 GPa. The rapid increase of the conductivity of NaCl solution may play an important role in many geological processes (such as the genesis of ore deposits under hydrothermal condition) and other fields.

Keywords: high pressure and high temperature, electrical conductivity, NaCl solution.

NaCl-H_2O is the most fundamental ternary system in geology. Knowledge of the physical and chemical properties of NaCl solutions is helpful for geologists to study Earth's interior geological functions and processes, for example, for geochemists to study the mechanism of ore deposition of elements, for seismologists to study the mechanism of earthquakes. Moreover, the study of electrode solutions under high pressure and temperature is also helpful for people in other fields, such as for those interested in the development of economic methods to obtain potable water from seawater by distillation methods and to develop and test new theories of ionic solution.

Probably the simplest and most direct method for obtaining information about the existence and behavior of ions in these solutions is the measurement of their electrical conductance[1]. Although conductance measurements on aqueous electrolyte solutions were made at temperatures up to 306℃ (at saturation vapor pressure) by Noyes and co-workers[2] early in this century, nearly 50 years elapsed before precise conductance measurements were extended into the supercritical region[3]. In 1956, Franck reported some results of his research on conductance measurements of aqueous solutions at 750℃ and 250 MPa[4]. Since then, Quist and Marshall[5] have measured conductance of aqueous solutions of K_2SO_4, $KHSO_4$, H_2SO_4 and NaCl at 400 MPa and 800℃. At present, it is still difficult to study the physical and chemical properties of aqueous electrolyte solutions under higher pressures because of limitation of experimental technique. Measurements of conductivity are mainly carried out on piston cylinder apparatus and are hardly carried out on cube-type apparatus. Therefore, measurements of conductivity are hardly made under higher pressures. In this work, the conductivity of 0.01 m NaCl solution was measured at 0.4—5.0

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GPa and 25—500℃.

1 Experimental

1.1 Apparatus

The experiments were carried out in a YJ-3000 ton press fitted with a wedge-type cubic anvil[6]. The pressure medium is pyrophyllite. The stainless steel heater was used. The cell assembly is shown in fig. 1. The conductance cell (with 12 mm in outer diameter, 4 mm in inner diameter, and 10 mm in length) was made of teflon, which does not react with water below 500℃ and has good insulation. The holes at two sides of the teflon tube were enlarged to 6 mm in order to place Pt tubes. Water was placed in the teflon tube with Pt tube seal. The electrodes of copper column were put into Pt tubes. Two wires were connected with ZLR-5 type apparatus to measure resistance. In order to avoid interference, 1-mm teflon flakes were placed between copper electrode and pyrophyllite column. A chromel-alumel thermocouple was also placed in the chamber to measure the temperature of the sample without any correction for the possible effect of pressure on the thermocouple emf. The measurement accuracy of the temperature was estimated to be 5℃.

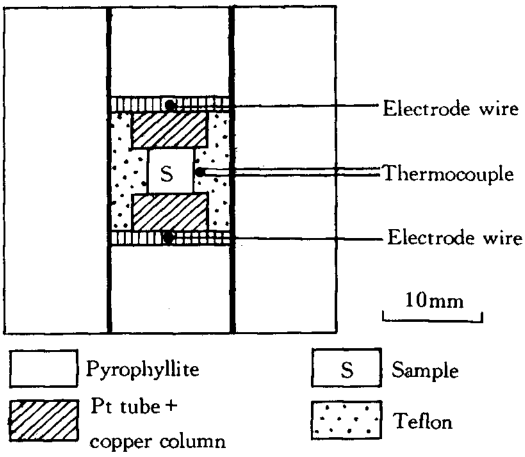

Fig. 1. Sample assembly of conductivity measurement.

1.2 Samples

The sodium chloride solutions were prepared gravimetrically from analytically pure reagent of sodium chloride (99.5% NaCl) and conductivity water. The conductive water was obtained by passing distilled water through a cation-anion-exchange resin. The electrical conductivity of water was 5.0 μS/cm at 11℃. So conductivity water makes little effects on the conductance of NaCl solutions.

1.3 Cell constant

Electrolyte solutions conduct current with cations and anions. The resistance of solutions is related to the number of ions in the solutions and the number of ions is related to the equilibrium constants of ionization. The conductance ability of electrolyte solutions is usually defined as the reciprocal of resistance (conductance)[7], that is $G = \kappa \times (A/l) = \kappa \times (l/Q)$, where κ is the conductivity, A the transverse area of the conductor or the area of the electrode to electrolyte solutions, l the length of the conductor or the distance between two electrodes and Q the cell constant (l/A). It is thought that the compressibility of the conductive cell is the same in different directions under high pressure. Thus, the cell constant at differential pressure and temperature can be calculated according to the density of NaCl solution. Since NaCl solution was dilute, its densities were assumed to be that of pure water and were calculated according to a Compensated-

Redlivh-Kwong (CORK) equation[8]. From these densities, the conductivity was calculated for each pressure and temperature.

1.4 Measurements of electrical conductivity

Electrical conductivity was measured using ZLR-5 type apparatus. The accuracy of this equipment was stated by the manufacturer to be better than 0.05%. The sample assembly was equal to a capacitance during measuring. The computer calculates the resistance of the sample according to all information.

Before experimental run, the conductance cell was rinsed with conductivity water. Experiment began at 0.4 GPa and then the pressure was increased until 5.0 GPa. At a certain pressure, the measurement was made after the equilibrium of 5 minutes at each temperature, and then the measurement was made at another higher pressure. In order to correct the effect of frequency, the conductivity was measured at frequencies of 1, 2, 4, 10 kHz, plotting these values against frequency and then extrapolating the plots to zero frequency when the conductivity was relatively low (such as the conductivity of solid NaCl solution) and conversely plotting these values against frequency ($f^{-1/2}$) and then extrapolating the plots to infinite frequency when the conductivity was very high.

2 Results and discussion

It is a key problem to determine the cell constant. The diameter and length of the cell were 4 mm and 3.95 mm, respectively. The electrode with cell constant 314.5 m^{-1} was used as the original conductance cell. The conductivity of 0.01 m NaCl solution measured by this method was about 100.65 μS/cm, which was consistent with 100.50 μS/cm measured by DDS-11A type conductivity apparatus.

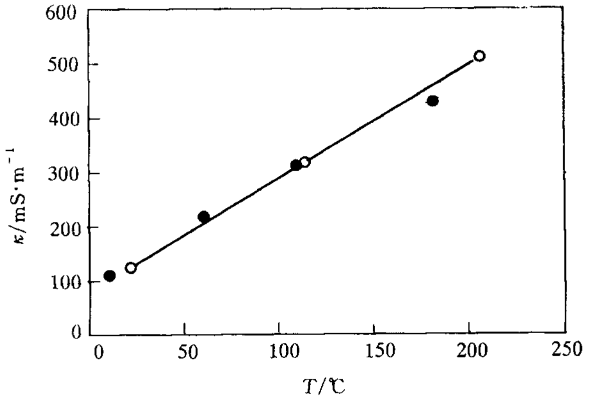

Fig. 2. The electrical conductance of 0.01 m NaCl solution as a function of temperature at 0.4—5.0 GPa. ●, This work; ○, reference [5].

Isobaric conductivity of 0.01 m NaCl solution as a function of temperature was calculated at 0.4—5.0 GPa and 25—500℃ according to the measurement resistance of NaCl solution (fig. 2). The results show that the conductivity of 0.01 m NaCl solution at 0.4 GPa is well consistent with that of Quist and Marshall[5] (fig. 3). The conductivity of NaCl solution increases rapidly with temperature at 0.4—1.5 GPa and below 500℃ (fig. 4). NaCl solution freezes into solid NaCl solution at low temperature and its conductivity is rather low. The conductivity of the solid NaCl solution increases slowly with temperature. However, it decreases before the solid NaCl solution melts. It may be a premelting effect of NaCl solution (fig. 3). As the solid NaCl solution melts, the conductivity of NaCl solution increases rapidly with temperature. The conductivity increases with temperature at lower temperatures and decreases slowly with increasing temperature at higher temperatures and decreases slowly with increasing temperature at higher temperatures and 2.0—3.0 GPa.

From fig. 2 it can be seen that the conductivity of NaCl solution changes little with increasing pressure at the same temperature below 1.5 GPa and increases fast with pressure above 1.5 GPa. This phenomenon can be explained from the behavior of water at constant temperature and high pressure studied using Monte Carlo simulation method[9]. The results from the hydrogen bond analysis showed that, as the pressure increases, the hydrogen bond strength decreases somewhat and the average number of hydrogen bonds increases[9]. Below 1.5 GPa, the properties of 0.01 m NaCl solution may be similar to that of water. Although increasing pressure will increase the number of ions in unit volume, the activity of ions decreases because of the hydrogen bonds increasing with pressure. This causes the conductivity of 0.01 m NaCl solution to be changed little below 1.5 GPa. The hydrogen bond strength continuously decreases as the pressure increases. When their strength decreases

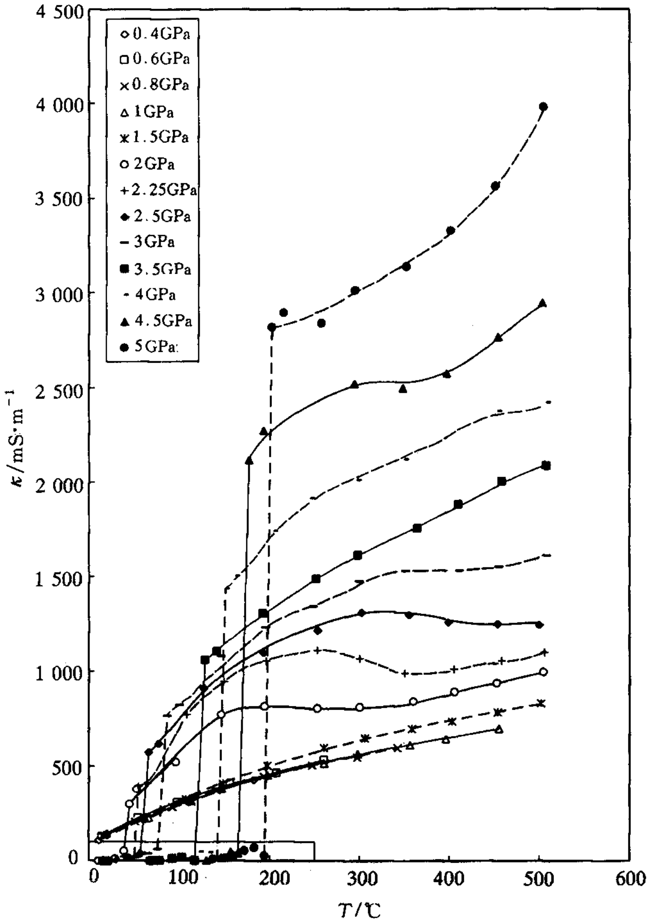

Fig. 3. The conductivity of 0.01 m NaCl solution as a function of temperature at 0.4 GPa.

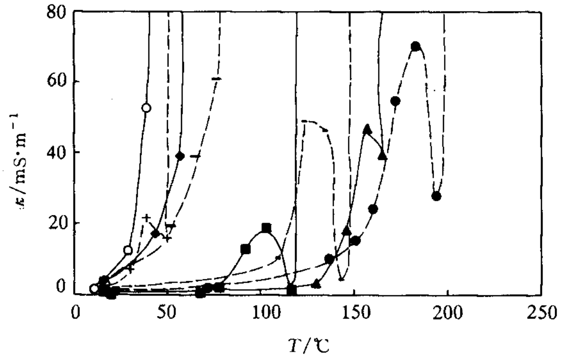

Fig. 4. The electrical conductivity of 0.01 m NaCl solution as a function of temperature (part of fig. 2, the legends are the same as in figure 2).

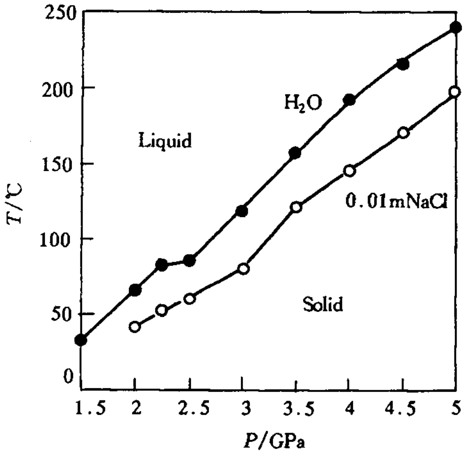

Fig. 5. The phase of 0.01 m NaCl solution.

to relatively small values, some hydrogen bonds break down and the number of hydrogen bonds decreases. Thus, the activity of ions increases; that is, the conductivity of solution increases. The higher the pressure, the less the number of hydrogen bonds and the higher the conductivity. This may play an important role in Earth's interior processes such as the genesis of ore deposit under hydrothermal conditions. It is commonly thought that ore elements are mainly transported as complex in hydrothermal solutions. The studies show that NaCl is the major component in hot brine and in the fluid inclusions of minerals and the NaCl solution can transport many ore elements under certain conditions. So NaCl solution plays a key role in the formation of some ore deposits.

The solid-liquid equilibrium of 0.01 m NaCl solution has a similar trend to that of water[10,11] (fig. 5) except that the temperature of solid-liquid equilibrium is slightly lower than that of water. This means that little impurity decreases the temperature of phase transition. If the equilibrium line of NaCl solution moves left by 0.5 GPa, it is basically the same as that of water.

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