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Abstract

Full Text

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V. B. PREOBRAZHENSKII, A. M. SUSOVA

CONDUCTIVITY OF AN ELECTROLYTIC NaCl SOLUTION IN HIGH-DENSITY WATER VAPOR

(Presented by Academician I. K. Kikoin on 17 VII 1964)

The study of matter in the supercritical state provides an exceptionally favorable opportunity to observe changes in the electrical properties of a condensed system with a gradual decrease in intermolecular distances.

In the course of carrying out a program for investigating the physical properties of matter in the supercritical temperature region, we measured the conductivity of an NaCl solution in water vapor with supercritical parameters.

It is known that water vapor at sufficiently high densities is an ionizing solvent and has the capacity to form electrolyte solutions. In work (^{1}) it was shown that NaCl solutions in water vapor are weak electrolytes and have an electrical conductivity of $0.73 \cdot 10^{-3}$ $\text{ohm}^{-1} \cdot \text{cm}^{-1}$ at the maximum vapor density attained by the authors, 0.4 g/cm^3, concentration $0.9 \cdot 10^{-3}$ mol/l, and temperature 393°; moreover, as was to be expected, the conductivity of electrolyte vapors depends strongly on density.

Fig. 1. Measuring circuit

Our measurements were carried out on a one-molal NaCl solution in water vapor in the range of vapor densities from 0.6 to 0.9 g/cm^3. The apparatus for measuring the conductivity of electrolytic solutions in high-density vapors consisted of a cylindrical high-pressure chamber with an internal channel 10 cm long and an internal diameter of 1 cm, into which a cell for measuring the conductivity of solutions was placed. The cell was made of platinum and had the form of a cylinder fitting tightly against the chamber walls. The inner surface of the cell served as one of the electrodes; the other electrode, also of platinum,

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

had a diameter of 2-3 mm and a length of 7-10 mm and was positioned coaxially with the first.

After a definite part of the cell volume had been filled with the solution under investigation, it was placed in the high-pressure chamber and, together with the chamber, heated to a specified temperature. In this case the vapor density in the region of single-phase states could be determined from the amount of solution placed in the cell and the total volume of the cell.

Sealing of the high-pressure chamber was accomplished by means of an obturator with an uncompensated area ([2]); rings of aluminum and annealed copper were used as gaskets. In the body of the obturator there is a channel through which the electrode passes, insulated from the channel walls by a porcelain tube. The electrical lead-in was sealed with polyvinyl chloride gaskets located in the cooled part of the obturator channel.

Electrical measurements were carried out using an alternating-current bridge (Fig. 1). Compensation was effected by varying the resistance R_1 and the capacitance C_1. The connection of the measuring cell into the bridge arm shown in the diagram, by means of two cables, substantially reduces the inductance of the lead wires, which distorts measurements at high frequencies in the resistance range from 5 to 0.5 ohm. The bridge was fed with an alternating sinusoidal voltage with a frequency from 1 to 20 kHz, which was necessary in order to eliminate polarization effects.

Fig. 2. Dependence of the specific resistance ρ of a one-molal NaCl solution in steam of density 0.9 g/cm^3 on temperature

In view of the small distance between the electrodes, polarization effects were relatively large. Polarization effects were eliminated by extrapolating the experimental curves of the dependence of resistance on frequency to infinite frequency. The frequency dependence of the measured resistance values is well fitted by a straight line on the frequency scale $1/\sqrt{\omega}$. Such elimination of polarization effects is theoretically justified [3].

Figure 2 shows a graph of the temperature dependence of the resistance of the solution at a steam density of 0.9 g/cm^3 up to temperatures of 480°. The curve was taken at a bridge supply-voltage frequency of 10 kHz. The errors associated with polarization effects amount, for this frequency, to as much as 20%. As can be seen from Fig. 2, at a solution density of 0.9 g/cm^3 a noticeable decrease in resistance with increasing temperature is observed.

Fig. 3. Dependence of the specific resistance of the solution ρ on steam density d

The dependence of the specific resistance of the electrolyte solution ρ on the steam density d is shown in Fig. 3. This dependence was obtained on the bridge at a temperature of 480° (in Fig. 3 the points were obtained by graphical extrapolation of the frequency dependence of the resistance, as described above).

To obtain the absolute value of the conductivity of the electrolyte-solution vapors, the conductivity values at given temperatures and densities were compared with the value of the conductivity of the same solution and in the same cell at room temperature and atmospheric pressure.

It is essential to note that the conductivity of an NaCl electrolyte solution in water vapor of density 0.6 g/cm^3 and temperature 480° is almost $2\frac{1}{2}$ times, and in vapor of density 0.9 g/cm^3 more than 4 times, greater than the conductivity of a one-molal solution under ordinary conditions. The specific resistance of a one-molal solution of density 0.9 g/cm^3 at a temperature of 480° is 2.5 $\Omega \cdot$ cm.

More detailed investigations are now being carried out. The authors express their deep gratitude to Academician I. K. Kikoin for great assistance and constant attention to the work, and to S. V. Kersnovskii for assistance in constructing the apparatus.

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Note: Figure translations are in progress. See original paper for figures.