STATE DIAGRAMS OF PHASE EQUILIBRIUM OF THE SYSTEMS SODIUM CHLORIDE–WATER, POTASSIUM CHLORIDE–WATER

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Abstract

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STATE DIAGRAMS OF PHASE EQUILIBRIUM OF THE SYSTEMS SODIUM CHLORIDE–WATER, POTASSIUM CHLORIDE–WATER

(Presented by Academician I. I. Chernyaev on 26 IV 1965)

At high temperatures and pressures in water-salt systems, in connection with the solubility of sparingly volatile substances in aqueous vapor, there exists yet another region characterizing the state of vapor solutions.

At the same time, the dissolution in aqueous vapor of sparingly volatile substances (salts) causes a strong change in the properties, in particular the volumetric properties, of the system; hence the complexity observed in the dependences that characterize the solubility of substances in aqueous vapor ([1]).

The investigation carried out for the experimental determination of data on the compositions of the vapor and liquid phases, specific gravities, pressures and saturation temperatures, distribution coefficients under phase equilibrium, and critical parameters for the systems sodium and potassium chlorides–water* made it possible, for the first time, to give state diagrams of phase equilibrium for systems with a volatile (water) and a sparingly volatile (electrolyte) component.

The experiments were carried out over a wide range of variation of the parameters: pressures from 1 to 400 kg/cm^2, temperatures respectively from 100 to 450°. In this case the concentration of the sparingly volatile component varied from 0 to values close to saturation under normal conditions.

The results of processing the primary experimental data are presented in the form of graphical dependences of the specific gravity of each of the phases and of the composition of the vapor phase** on the boiling (saturation) temperature of liquid solutions of constant compositions, expressed by lines of isoconcentration. Pressure, expressed by isobar lines, was also chosen as a constant parameter in the graphs.

In Fig. 1A a p—$\gamma(v)$—t—C diagram is presented for vapor-liquid phase equilibrium of the sodium chloride–water system; in Fig. 1B the same is presented for the potassium chloride–water system.

Figure 1. Phase-equilibrium diagram of the system NaCl–H_2O (A) and the system KCl–H_2O (B)

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The upper part of the diagram, located above the water saturation line and the critical line, characterizes the state of boiling aqueous solutions of sodium and potassium at various compositions, pressures, and temperatures.

The lower part of the diagram, bounded by the saturation line of water vapor, the critical line, and the line of saturated vapor solutions, represents the state of aqueous-vapor solutions of these salts that are in equilibrium with boiling aqueous solutions of various composition at various temperatures (pressures).

The range of parameters investigated also encompassed the critical region of the systems. In the experiments, the parameters of the critical state were recorded, where all properties of the vapor and liquid phases become identical. The geometrical locus of these parameters on the diagrams forms segments of critical lines.

* That is, systems having a positive temperature coefficient of solubility.
** The composition of the vapor phase is determined by the distribution coefficient of the dissolved salt between the vapor and liquid phases (see Fig. 2).

The complete diagrams, obtained for the first time, of the state of aqueous and vapor solutions of sodium and potassium chlorides show the general form of the state diagram p—$\gamma(v)$—t—C, typical for two-component systems with components that differ in volatility; in particular, also for systems water (volatile component) –salt–electrolyte (slightly volatile component).

Fig. 1. Phase-equilibrium diagram of the system NaCl–H_2O (**A**) and the system KCl–H_2O (**B**)

Characteristic of such systems is that the two-phase vapor–liquid region and their critical region extend over a wide range of parameters, beginning at the critical point of water. The strongest changes in the properties of the systems with increasing salt concentration are observed near the critical line. At the same time, the intensity of the change of the parameters with temperature (the magnitudes of the derivatives with respect to temperature),

characterizing the phase transitions near the corresponding critical points decreases as the proportion of the less volatile component in the system increases.

Figure 2 presents isotherms of the distribution coefficients of sodium chloride and potassium chloride between the vapor and liquid phases of systems, showing the nature of the changes in the phase-equilibrium constant with composition for systems with components of different volatility.

Fig. 2. Isotherms of the distribution coefficients of NaCl between the vapor and liquid phases (I), the same for KCl (II)

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Fig. 2. Isotherms of the distribution coefficients of NaCl between the vapor and liquid phases (*I*), the same for KCl (*II*)

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1. M. A. Styrikovich, I. Kh. Khaibullin, DAN, **109**, No. 5, 962 (1956).

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