Strategy, methods and equipment for experimental studies of water–salt systems under superambient conditions

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ABSTRACT This paper presents a breif description of various experimental methods for hydrothermal phase equilibria investigations. Its second part includes some recommendations on the strategy of experimental studies of binary and ternary water-salt systems under superambient conditions. This work is an application and continuation of the previous work on phase behaviour discussed earlier in this Journal (Pure & Appl.Chem. 63, 2129 (1990))

Water-salt mixtures are present in many industrial hydrothermal processes as well as in natural environments and the need for thermodynamic data under superambient conditions, that is at high temperaure and pressure, is still growing. Ordinary experiences rarely can give even rough information about the phase constitution of hydrothermal systems. The need for these data comes from very different groups, ranging from chemists, geologists and oceanographers, to the chemical industry and fossil- and nuclear-power engineers, and to the specialists of environmental chemistry. The main source of data on water-salt equilibria under superambient conditions is from experimental investigation.

Modern theoretical approaches are not able to predict the thermodynamics and phase behaviour of binary and ternary water-salt systems. But, if such information about simple systems is available, the thermodynamic calculation of multicomponent equilibria, being extremely important for modeling of industrial and natural processes, becomes possible (1-3). The present approach eliminates some problems of experimental studies, because the investigations can be limited to binary and ternary systems. But even for simple systems experimental measurements of hydrothermal equilibria in a range of P-T-X parameters are still so specific, complicated and time-consuming, that for systematic investigations, it is desirable to formulate some guiding principles (besides special equipment and methods), that would allow one to decrease the amount and increase the performance of experiments.

The goals of this article are:
- to give a brief review of modern experimental methods for the investigation of hydrothermal phase equilibria;
- to demonstrate how the analysis of complete phase diagram constructions makes it possible to formulate a strategy for experimental studies and to interpret the results of the measurements.

EXPERIMENTAL METHODS AND EQUIPMENT

In an article of this size it is not possible to discuss in detail all specifications and technical improvements which have been used for hydrothermal studies. There exists extensive literature (4-6) on experimental techniques at high pressures and temperatures, that describes the materials used, special equipment, unit parts and design of some apparatus. Here we shall be primarily concerned with the major features of experimental methods used for the investigation of solubility phenomena in aqueous systems under superambient conditions.

Experimental methods of hydrothermal equilibria studies may be divided into five groups which differ in technique of obtaining the information on phase state of the systems and on coexisting phase

compositions at high temperatures and pressures:
1. Methods of visual observation of phase equilibria.
2. Methods of sampling of phases at experimental conditions
3. Methods of radioactive tracers
4. Methods of quenching of high temperature phase equilibria.
5. Indirect methods - determination of discontinuity ("break points") in the curves, describing a behavior of interdependent parameters and (or) properties of the system at a moment of phase transformation.

METHODS OF VISUAL OBSERVATION enable the determination of the phase constitution of a system and parameters of phase transformation, recording the appearance (disappearance) of phases and critical phenomena with changing temperature and pressure.

At pressure up to 15-25 MPa, thick-walled capsules (6-3 mm o.d., 2-0.8 mm i.d., 2.5-5 cm length) placed into the heating devices, may be used (7-9). The capsules are made of transparent fused silica (7,8) or Pyrex glass (9) capillary tubes. The known quantities of solid and liquid phases are introduced into the capsule, then it is frozen (in liquid nitrogen), evacuated and sealed.

Visual polythermal capsule studies of aqueous systems conducted to temperature of 400-480°C do not yield any information about the pressure. The influence of the capsule wall dissolution on the composition and properties of a system under consideration is another complicated problem. The reproducibility of temperature determination of such phase transitions as liquid immiscibility or critical phenomena, is in the range of several tenths of a degree for the best measurements. Most of salt solubility measurements have an error of ±1-2°C.

At pressures above 15-25 MPa, stainless steel vessels with sapphire (10,11) or quartz (12) windows are used for visual observation. Such apparatus allows one to combine the observation of the phase relations in a system with the registration of both temperature (with the accuracy of ±0.2-1 K) and pressure (with the accuracy of ±0.1-1 %) for sysem temperature up to 500°C and at pressures up to 350 MPa. The volume variation of high-pressure reactor is also possible in some apparatus (11), where a piston separates the heated reactor from low-temperature part of the installation.

The diamond cells are also used for studying solubility phenomena at very high pressures (up to 900 MPa) (6).

METHODS OF SAMPLING are often used for studying the hydrothermal equilibria and have a wide range of designs. Samples can be withdrawn during a high P-T run either by flow methods of sampling or by static withdrawal of an aliquot of fluid.

The flow methods involve pumping a fluid into a reaction vessel slowly enough so that the desired temperature and reactor period can be maintained while simultaneously leaking an equivalent volume through a restricted vent (4,6,13). Unfortunately the quality of the sample is always in doubt because, as noted by H.L.Barnes (5), the reaction cannot be unequivocally reversed and equilibrium is not assured. In addition, simply slowing the flow rate, until concentration in the effluent is unaffected by the rate, only demonstrates that a steady state has been achieved. Nevertheless some equilibrium data (for example, salt solubility in steam (13)) have been obtained by flow methods. An advantage of flow methods is that large samples can be collected.

Most of the data on solubility phenomena in aqueous systems at high temperatures and pressures have been obtained by static sampling methods. The design of the simplest version of an apparatus for studying equilibria L-G-S, L-G and G-S by method of sampling includes a heated thick-walled stainless steel vessel (in which the equilibrium of a charged mixture is reached) with capillaries (which can be fitted out with a filter) and valves for sampling a portion of solution from high-pressure reactor into the region of atmospheric pressure and room temperature (14,15). The main problems of using this version of apparatus with sampling are related to the fact that the portions of the high-temperature solution are subjected to the simultaneous drop of both pressure and temperature during sampling. The resulting crystallization and boiling processes may lead to considerable changes of the sample composition. Therefore, the strong limitations are imposed on the possibilities of using the above-mentioned equipment in relation to temperatures, concentrations of solutions being sampled and volume of samples. The use of such apparatus is most promising when studying the solubility of slightly-soluble compounds, the diluted solutions of which tend to supersaturation, and in the case of compounds that have a negative temperature coefficient of solubility.

Some of the above-mentioned problems were solved by using a hermetic sampler which is a component of the hydrothermal bomb construction placed in a hot part of the apparatus (16-20). The empty sampler vessel is isolated from the main vessel of the bomb by a valve needle (the sealing system is placed in the hot part of the setup) until the equilibrium is established. The sampler channel is opened

for a few minutes and the liquid phase, passing through a dense filter, is injected into the empty sampler. Stainless steel mesh or frit (5,18), sintered teflon (15), porous ceramics (19) and a fine silver wire (16), that are pressed into the sampler channel, are used as filtering materials. The presence of vapour phase compensating the increase of the system volume with the sampler opening makes the use of this apparatus. This provides the accurate determination of salt solubility in liquid solution at temperatures and pressures where the salt solubility in the vapour may be neglected and where an estimate of the amount of water passing into vapour may be made.

It is evident that an optimum method of sampling is achieved if the procedure of sample withdrawal is accompanied by no change in either temperature or pressure. This can be rather easily attained in the case of the determination of high-temperature phase compositions in equilibrium L-G using the hydrothermal bomb with two chambers connected by a narrow aperture that can be closed by a valve for separation of one phase from another (21,20). The main design feature of this type of apparatus for the determination of salt solubility (21,22) is a device for breaking off the contact of the crystals with the solvent, for example, by repositioning the crystals from liquid solution into vapour. where the solid phase solubility is negligible. Usually the crystals are transferred from liquid to vapour and backwards by means of rotating the bomb (22). A separation of solid and liquid phases can be achieved by centrifugation of a two-chamber autoclave and closure of the aperture between chambers at high temperature (19) or by isolation of a part of the solution volume in the high-pressure vessel with special devices (28). A new method of the same type uses synthetic inclusions formed by healing fractures in quartz for sampling the hydrothermal solution at high temperatures (up to 1000°C) and pressures (up to several hundred MPa) (6).

High-temperature isopiestic technique (23,24) may, at a stretch, be attributed to the experimental equipment for studying liquid-gas equilibrium by the method of sampling.

METHODS OF RADIOACTIVE TRACERS for studying the solid phase solubility in high-temperature aqueous and vapour solutions, allow one to conduct a continuous determination of the hydrothermal fluid concentration by measuring the intensity of radioactive radiation without sampling. This is an advantage of such methods. Other advantages are their high sensitivity, selectivity and the ability to determine the compositions of rather diluted solutions with an error of ±2.5-5% . At the same time, it should be kept in mind that an isotope must be a gamma-emitter of rather high radioactivity, so that the radiation from the low concentration of the isotope can be detected by a counter outside the bomb. The isotope must be rather durable, lasting for a month or longer. In addition there are complications from the problems of hydrothermal equipment resulting in dangerous experimental studies when such apparatus are used. Nevertheless, the determination of solubility with this method is described in (4,25).

METHODS OF QUENCHING are based on the ability to fix and maintain the phase assemblage present during a run at high temperatures and pressures by mean of fast cooling and subsequent studying the quenched phases at normal conditions. Such methods are acceptable for studying systems with low rates of phase reactions. Systems with high-temperature liquid phases being quenched in glass are the most favorable. Therefore, methods of quenching are widely used in mineralogy and petrography for studying high-temperature equilibria in aqueous systems with silicates and aluminosilicates. A considerably wide range of parameters (up to 1000-1200°C and 1000-1500 MPa) may be studied by methods of quenching, using cold-sealed and internally heated pressure vessels in which sealed thin-walled platinum (gold) capsules with water-salt mixtures (volume of 0.05-1 cub.cm.) are placed (4-6). A very important feature of capsule techniques is the opportunity to use buffering techniques for hydrothermal systems when either fugacity or activity of a system is controlled by additional phases (buffers) placed in the charge capsule or in the other capsule (5,6).

Some saturated solutions of slightly soluble compounds with low salt concentrations can maintain the supersaturation occurring during an abrupt cooling of the system. This phenomenon is used in quenching versions of the weight-loss methods in which a dissolving crystal is not isolated from the solvent. Such solubility determinations are carried out in quenching high-pressure vessels (Morey type bombs (26)) with volume of 50-500 cub.cm. at temperatures up to 450-500°C and pressures up to 100 MPa (12). But it should be kept in mind that the quality of these solubility data always raises doubts and requires the most careful analysis of products and a special study of interactions between cooled solutions, crystals and quenching phases.

The essence of so called "INDIRECT METHODS" is that measured system characteristic dependence upon a varied parameter changes with a transition from one phase state to another at the appearance or disappearance of a new phase. Accordingly, the P-V-T-X curves (pressure as a function of temperature; pressure or temperature as a function of volume; pressure drop during salt dissolution as a function of

Fig. 1. Systematic classification of the main types complete phase diagrams for binary systems, in P-T projections.

Diagrams in frames: boundary versions of diagrams with high-order invariant points LN, RN, pR, pQ, MQ.

Thin lines: monovariant curves of one-component systems.

Thick lines: monovariant curves of binary systems.

Dashes lines: critical curves.

Dotted lines: metastable parts of monovariant curves.

Filled points: invariant points of one- and two-component systems.

The main types of phase diagrams are denoted by a figure (1 or 2) and a letter (a, b, c, d), whereas the boundary versions are denoted by three symbols (two figures with a letter, or a figure with two letters)

salt concentration) will break at a moment of phase transformation. The details of experimental procedures for method of P-V-T-X curves as well as the equipment are described in (11,16,27-29).

The studies of temperature, pressure and concentration dependence of various properties (such as density (30), electroconductivity (31), etc) of water-salt systems or individual phases, show that the phase transformation is sure to manifest itself in a change of the curve.

Differential thermal analysis (DTA) is also an example of the method of "parameter-property" curves, where the thermal effect is a measured property of a system with temperature and time as parameters. The applications of DTA to hydrothermal systems were extensively developed, mainly in geochemical and chemical investigations (20,32-34).

STRATEGY OF PHASE EQUILIBRIA STUDIES

Any preliminary information about results of measurements makes it possible to select the method of investigation and to plan the experiments. In the case of high-temperature water-salt equilibria such information becomes especially important because besides the technical problems, the hydrothermal equilibria are highly diverse, specific and considerably different from solubility phenomena in the same systems under ambient conditions. At temperatures up to 100-200°C and different pressures the diversity of heterogeneous equilibria is mainly due to the abundance of crystalline hydrates. At higher temperatures and pressures in hydrothermal conditions, the crystalline hydrates disappear, but liquid-liquid immiscibilities, critical phenomena and super-critical equilibria, nonexistent at lower temperatures, are wide-spread. Therefore the main focus in experimental investigation of hydrothermal systems should be on the examination of fluid equilibria.

Water-salt mixtures belong to a large class of systems consisting of components with different volatility, where water is always the volatile component and the salt (non-volatile) components are represented by any inorganic compound with high melting temperature and low vapour pressure. Available experimental and theoretical data for such systems can be accumulated in the form of main types of complete phase diagram describing all the equilibria that are possible in the system with participation of gas (G), liquid (L) and/or solid (S) phases throughout the entire range of parameters at which the non-crystalline phases remain heterogeneous.

The method of continuous topological transformation of phase diagrams permits one to obtain for binary mixtures the systematic classification of complete phase diagrams, including both known types and new ones, derived in a frame of definite limitations (16,35). The new version of such classification including 1st, 2nd, a, b, c, d types of complete phase diagrams is given in Fig. 1. By use this method and the main types of phase diagrams it is possible to remove the limitations one by one, and to deduce phase diagrams of any degree of complexity. An example of such derivation can be found in (16).
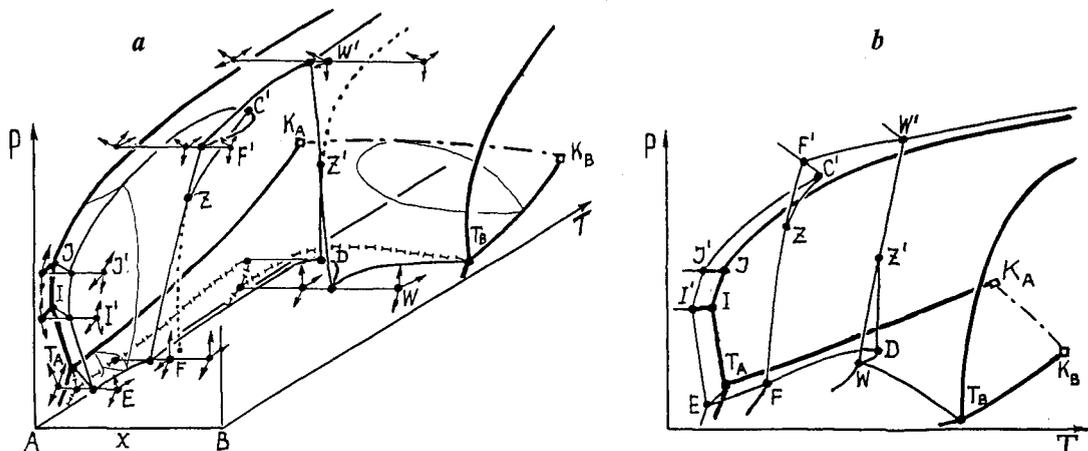

Fig. 2. P-T-X (*a*) and P-T (*b*) schemes of complete phase diagram for the binary system A-B of the 1st type with polymorphism of component A and with binary compounds C, D.
Thick lines: monovariant curves of one component systems; thin lines: monovariant curves of binary system; dashed lines: compositions of vapour (gas) in 3-phase equilibrium G-L-S; dash-dotted lines: critical curves; dotted lines: metastable part of melting curves of binary compounds; points - invariant equilibria; points with arrows: compositions of solid in invariant equilibria.

Fig. 2 shows another example, where the scheme of phase diagram for the 1st type system is characterized by polymorphism of component A and by the formation of two binary compounds (crystalline hydrates). Equilibria with crystalline hydrates as well as ice polymorphism are very common for water-salt systems. Futher, this diagram demonstrates general phase behaviour under very high pressures for any kind of binary system, where all the compressed fluids are crystallized.

At vapour and not very high pressures the binary compound C melts incongruently whereas the compound D has the stable congruent melting point D. The incongruently melting compound C transforms into the congruently melting one with pressure increasing, whereas the compound D reaches incongruent melting relations at higher pressure. This occures at the points Z and Z', where the variable composition of solution saturated with two solid phases (curves FF' (L-Sc-Sd), WW'(L-Sd-Sb)) coincides with composition of the binary compound. The solubility curve (EFDWTb) of 3-phases equilibria L-G-S running from E (L-G-Sa'-Sc) to triple point Tb, are divided by two invariant peritectic F (L-G-Sc-Sd) and eutectic W (L-G-Sd-Sb) points into three branches with the solid phases C, D or B of different composition. The shape of solubility curve (L-G-S) of the congruently melting compound must always have a temperature maximum and may or may not have a pressure maximum.

The intersection of the solubility surface of equilibrium L-Sa with the solubility surfaces of the equilibria L-Sc, L-Sd and L-Sb gives the monovariant eutectic curve EI'J'C'F'W' of solutions saturated with two solid phases. This eutectic curve, as the solubility curve EFDWTb, has a temperature maximum at the intersection with a stable part of the congruent melting curve ZC' of the binary compound C. The vapour pressure of the solubility curve EFDWTb decreases with increasing solution concentration after the temperature maximum at the point D whereas the pressure of the monovariant eutectic equilibrium L-Sa-Sc increases with increasing solution concentration after the temperature maximum at the point C'. Hence the eutectic curve has to have a temperature maximum (see branch J'C'F') when the composition of liquid phase coincides with the composition of the binary compound.

The scheme of classification of binary phase diagrams (Fig. 1) may also be used to derive complete phase diagrams of ternary systems, if the phase diagrams of boundary binary systems are known (16,35).

Theoretical derivation of topological schemes for phase diagrams of two- and three-component systems as well as the experimental data on water-salt equilibria in a wide range of parameters provides a fundamental basis for formulation a strategy of experimental studies of hydrothermal systems. The main idea of the strategy is to obtain first the experimental data that would allow one to choose the type of phase diagram corresponding to the system under consideration from all possible theoretical types of diagrams.

BINARY SYSTEMS. In the case of a binary water-salt system investigation the following sequence of experimental procedures can be proposed.

The first stage of investigation is to attribute the studied system to the 1st or to the 2d type. Systems of the 1st type have a positive temperature coefficient of solubility (t.c.s.) in the three-phase equilibrium L-G-S and exhibit no critical phenomena L=G in solutions saturated with solid. Systems of the 2nd (p-Q) type have negative t.c.s. in the subcritical L-G-S equilibrium and also show critical phenomena in saturated solutions (critical end-points "p" and "Q").

The determination of the 1st or the 2nd type of binary systems is possible if solubility measurements are conducted up to melting temperature of salt component or, at least, to 400°C. If, at temperatures about 374°C, the concentration of a substance in liquid phase increases with heating, diverging from the composition of equilibrium vapour solution, such system belongs to the 1st type. On the contrary, the reduction of solubility with heating in the vicinity of the critical temperature of water and convergence of liquid and vapour compositions, indicate that the system belongs to the 2nd type.

The presence of a maximum vapour pressure of saturated solution which is found when heating the system in the conditions of the three-phase equilibria (G-L-S), indicates unambiguously that the system belongs to the 1st type.

Another sufficient criterion for attributing a system to the 1st type is the occurence of critical phenomena G=L in the wide range of parameters corresponding to the part of the critical curve starting from the critical point of water.

The most obvious feature of the 2nd type systems is the occurence of critical phenomena between liquid and vapour phases in the presence of a solid phase at temperatures slightly exceeding the critical temperature of water, i.e. invariant critical point "p". This phenomenon is observed visually in sealed glass tubes or other equipment of this kind, when heating the system in the three-phase state (L-G-S)).
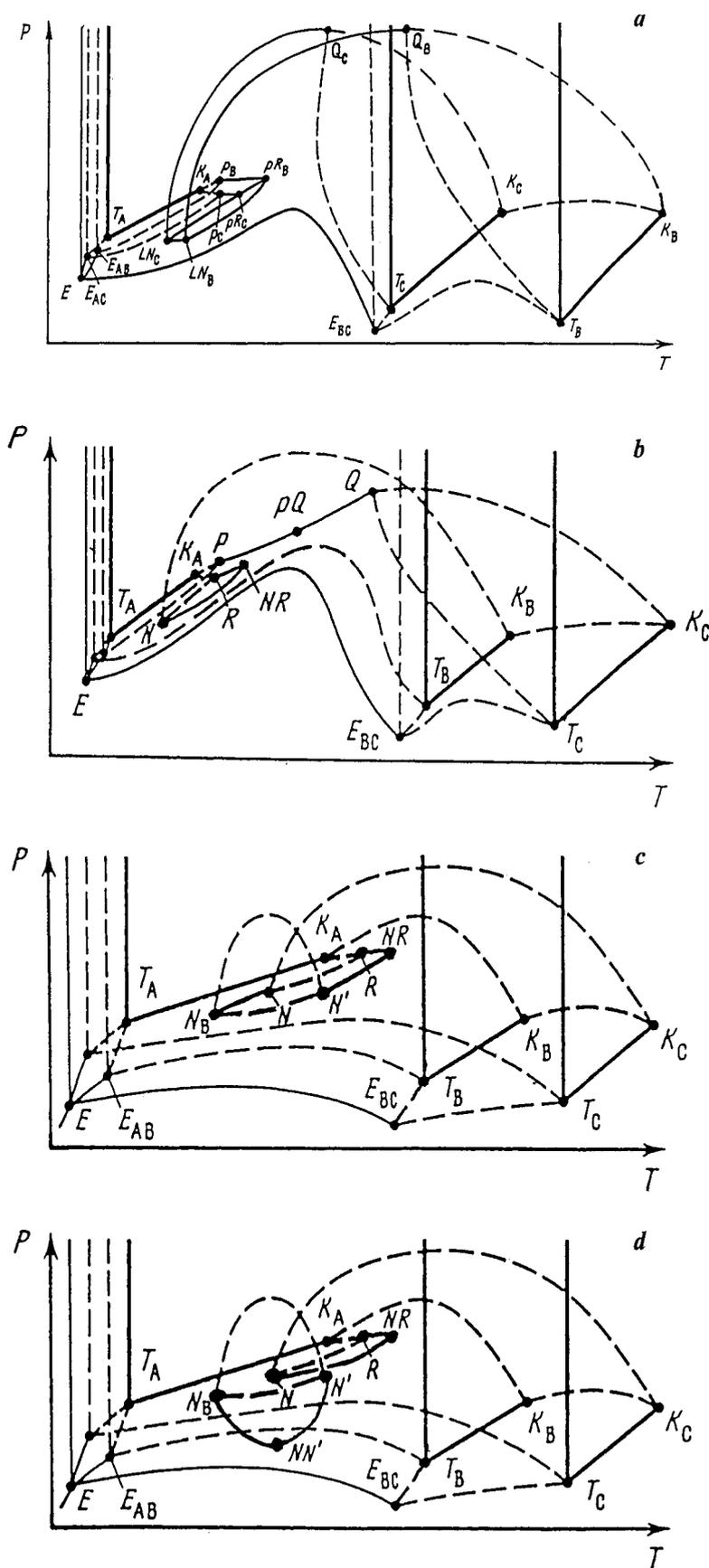
Fig. 3. P-T projections of complete phase diagrams for the ternary systems.

a - both boundary binary systems with volatile component (A) belong to the 2c'-type; continuous transformation of quasi-binary sections: 2c'-12c'-1c'-1c'c-1c-1c'c-1c'-12c'-2c' (see Fig. 1).

b - binary system A-B belongs to the 1c-type and system A-C - to the 2a-type; continuous trans formation of quasi-binary sections: 1c-1ca-1a-12a-2a (see Fig. 1)

c and d - the same types of boundary binary systems (A-B - the 1b-type; A-C - the 1c-type) but different phase bahaviour in the region of 3-component composition. The immiscibility regions of boundary systems are united into one (Fig. 3c) with the following continuous transformation of quasi-binary sections: 1b-1bc-1c. The immiscibility regions of boundary systems are separated by the 3-component region of miscibility (Fig. 3d) with the following continuous transformation of quasi-binary sections: 1b-1ab-1a-1ac-1c.

Points are the invariant equilibria.
Lines are the mono-variant curves for one-(thick lines), two-(dashed lines) and three-(thin lines) component systems.

The second stage of experimental investigation is the determination of the existence and type of the immiscibility region in the given system. Available experimental data for water-salt mixtures show that 3-phase region of immiscibility (L1-L2-G) can be found only at temperatures higher than 200-250°C.

Two types of immiscibility regions have been established in the experiments: limited immiscibility region with the critical curve L1=L2, which does not intersect the critical curve L=G (the b-type of phase diagrams in Fig. 1) and the region of liquid-liquid immiscibility with a continuous transition into the liquid-gas equilibria and with an intersection of critical curves L1=L2 and L=G (the c-type of phase diagrams in Fig. 1). Two other exotic forms of immiscibility region ("Schneider egg" (36) in the d-type of phase diagrams (Fig. 1) and the equilibrium L1-L2-G in which vapour pressure decreases with heating in the e-type of phase diagrams (Fig. 1) are assumed only (16,35,36) but have no experimental examples.

The detection of a metastable three-phase immiscibility in the 2nd type systems (2c' type in Fig. 1) is a more complicated problem. To solve it, a careful analysis of stable phase equilibria and determination of their peculiarities are necessary. The criteria of the 2c' type systems are as follows:
1. The parameters of the critical point Q and neighboring parts of the curves QTb and QKb are characterized by the pressure values which are considerably higher than those of the supercritical transition of water from gas-like to liquid-like state at the same temperatures.
2. The extrapolation of the critical curve QKb to the region of lower temperatures (in the vicinity of Ka) in T-X projection of phase diagram leads to a region of the compositions of supersaturated concentrated solutions rather than to a critical point of the volatile component (water) Ka.
3. The P-T projection of the three-phase equilibria L1-L2-Sb and G-L-Sb (QTb curve) in some systems has a characteristic inflexion (band) and sometimes even a temperature minimum corresponding to gradual transition of equilibrium G-L-S to equilibrium L1-L2-S with increasing pressure.
4. The temperature of critical point Q (L1=L2-S) may be either higher or lower than that of critical point p (G=L-S), while the pressure at point Q is always higher than that at point p.

TERNARY SYSTEMS. It is reasonable to start the experimental investigation of ternary system after the determination of the types of boundary binary systems and the theoretical derivation of possible versions of complete phase diagram for the ternary one is accomplished. A large body of ternary phase diagrams does not allow one to formulate a single way for experimental investigation of water-salt systems under hydrothermal conditions. But there are some general regularities of phase behaviour in ternary systems that can be used in the design of experiments for the determination of the phase diagram type of the system considered. Some examples of complete phase diagram for ternary systems are given in Fig. 3.

The solubility surfaces of the three-phase equilibrium (L-G-S) in ternary water-salt systems exhibit some regular trends such as a decreasing of P-T parameters when concentration of the second salt, which is absent in equilibrium as phase, is increased. This general feature of solubility behaviour for all solid phases of constant composition results in a special form of the solubility surface of a ternary system having the singular minima at eutonic and eutectic solution compositions. The eutonic and eutectic equilibria (points E and curves EEbc in Fig. 3) are characterized by the highest concentrations at a given temperature and pressure, by minimum vapour pressures in isothermal cross-sections, by extreme pressures in isothermal sections and by the lowest temperatures in isoconcentration (isopleth) sections of phase diagrams.

The divariant critical surfaces of ternary systems inherit the forms of critical curves of boundary binary systems and do not have such features as solubility surfaces in the region of eutonic and eutectic compositions. Different behaviour of the critical surface and the solubility surface on passing from boundary system of the 2d (p-Q) type to the eutonic compositions of a ternary system may or may not result in a considerable change of phase equilibria. The obligatory reduction of P-T parameters of solubility surface on approaching eutonic compositions may be so significant that the intersection of critical (L=G) and 3-phase (L-G-S) equilibria discontinues, the critical phenomena in saturated solutions (L=G-S) disappear and phase behaviour becomes similar to that in the binary systems of the 1st type. In other words it can happen that the quasi-binary eutonic section will have a phase diagram of the 1st type although both boundary water-salt systems belong to the 2nd type.

In the case of boundary binary system of the 2nd type with metastable region of liquid-liquid immiscibility (the 2c'-type in Fig. 1), the disappearance of critical phenomena in a saturated solution (curves QbLNb, QcLNc, pbpRb, pcpRc in Fig. 3a) as well as 1st type behaviour of eutonic solution (curve EEbc) is accompanied by the transition of the 3-phase region of immiscibility (L1-L2-G) to stable equilibria (field pRbpRcLNcLNb in Fig. 3a).

If the boundary water-salt systems of a ternary system belong to the 1st type with limited liquid miscibility of saturated solutions, the obligatory reduction of P-T parameters of solubility surfaces

promotes the transition of the metastable parts of the immiscibility region into a stable condition at eutonic compositions. The nonvariant equilibria LN (L1=L2-G-S) or pR (L1=G-L2-S) arise in the three component region of compositions in these ternary systems.

The general features of ternary systems with boundary water-salt systems of different types (1st type system A-B and 2d type system A-C in Fig. 3b) are the change of the sign of temperature coefficient of solubility (t.c.s.) from negative to positive with increasing salt concentration and the disappearance of critical phenomena in saturated solutions (monovariant critical curve QpQp (G=L-Sc) characterized by the low concentrations of B in critical solutions). The negative t.c.s. typical for the hydrothermal solutions of the 2nd type changes into a positive one when the solution composition has lower than 10-15 mol% of salt which forms the system of the 1st type with water (16,35).

When one of the boundary water-salt system belongs to the 1st type with immiscibility region of c-type and the immiscibility of liquids is absent in another binary water-salt system (see Fig. 3b) the nonvariant equilibrium NR (L1=L2=G), the so called "tricritical point", will be found in the region of the three component composition in such ternary systems.

If the boundary water-salt systems belong to the 1st type with different types of immiscibility regions (b- and c-types), the topological transformation gives two versions of the phase diagram for such a ternary system. In one case (see Fig.3c) the immiscibility region spreads from one boundary binary system to another with a continuous transition from the b-type into the c-type through the nonvariant tricritical point NR (L1=L2=G). There are two immiscibility regions adjacent to the boundary binary systems separated by a region of miscibility in the other version (see Fig. 3d). It is interesting to note that the first version of phase transformation does not follow from the theoretical analysis of equation of state (37,38) that predicts only the second version of phase transitions.

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