

Citation:

Lobry de Bruyn, C.A. & A. Smits, The occurrence of an upper critical point of mixing at the coexistence of two mixed crystal phases, in:

KNAW, Proceedings, 16 I, 1913, Amsterdam, 1913, pp. 557-564

Chemistry. — “The occurrence of an upper critical point of mixing at the coexistence of two mixed crystal phases.” By Prof. A. SMITS and C. A. LOBRY DE BRUYN. (Communicated by Prof. J. D. VAN DER WAALS).

1. When examining the system KCl — NaCl KURNAKOW and ZEMCZUZYNI¹⁾ found that as Fig. 1 shows, a continuous melting-point line occurs here with a temperature minimum at $\pm 664^\circ$, and that after the solidification a transformation still makes its appearance in different mixtures.

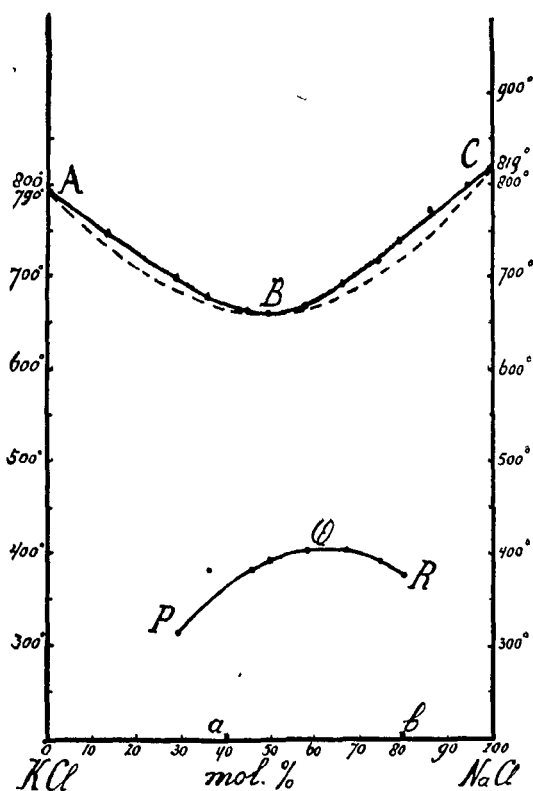


Fig. 1.

The existence of these transformations (which is chiefly of interest here) has appeared in two ways. In the first place from the curves of cooling and in the second place from the fact that, as was first found by OSTWALD²⁾ and BEKETOFF³⁾, and afterwards confirmed by KURNAKOW and ZEMCZUZYNI, the heat of solution of a mixture

¹⁾ Z. f. anorg. Chem. 52, 186, (1907).

²⁾ Journ. prakt. chem. 25, 8 (1882).

³⁾ Z. f. anorg. chem. 40, 855 (1904).

which has *suddenly* been cooled from a temperature above 407° to 0° , differs considerably from that of a mixture that has been allowed to cool down *slowly*. In case of rapid cooling the heat of solution appeared namely to be much smaller negative, which points to an exothermal process, which failed to appear in case of rapid cooling. After continued heating at 85° — 150° the negative value of the heat of solution rose, and after a few days it had acquired the value of the mechanical mixture.

It was on the ground of these phenomena that K. and Z. concluded that the isomorphous mixtures are decomposed at 300° — 407° , so that solid solutions are formed, which already at 100° — 150° consist almost exclusively of the components.

This conclusion is also optically confirmed, for as OSTWALD already observed, the suddenly cooled mass gives the impression of white enamel, whereas the salts taken separately yield a perfectly transparent solid substance when the melt is cooled. On slow cooling it is now clearly observable that the enamellar substance is converted to a transparent mass.

Though in these experimental data clear indications are to be found for the probable explanation of the observed phenomena, and this explanation is easy to test, KURNAKOW and ZEMCZUZYNI have evidently not realized this, for they conclude: "Weitere Untersuchungen müssen zeigen, ob die Zersetzung der festen Lösungen von Erscheinungen des Polymorphismus oder von anderen Ursachen abhängt." As however these "weitere Untersuchungen" seem not to have been undertaken by K. and Z., and as the question under discussion is an exceedingly important one, which can be answered in a simple way, we undertook the following investigation.

2 OSTWALD's experiments and those of KURNAKOW and ZEMCZUZYNI about the heat of solution show that the stable state of equilibrium at the ordinary temperature is most probably an equilibrium of two mixed crystal phases, one of which consists practically of *KCl*, and the other of *NaCl*.

If this be true, we meet here with the interesting case that at higher temperature these coexisting mixed crystal phases approach each other more and more in concentration, and become perfectly identical at 407° , or in other words they exhibit an upper critical mixing-point.

The top of the line *PQR* in Fig. 1 lying at about 66.6 mol. % *NaCl*, the possibility of the occurrence of a compound might, however, also be thought of. It should be noted, however, that not a single

fact pleads in favour of this supposition, but that on the contrary the observed phenomena make this supposition highly improbable. Nevertheless it is here of some importance to consider also this case, in which the curve PQR then would indicate in what way the temperature of the transformation homogeneous mixed crystals \rightarrow mixed crystal phase + compound varies with the concentration.

To arrive at perfect certainty about the interpretation of the phenomenon, the ternary system $H_2O - NaCl - KCl$ was studied at 25° and atmospheric pressure, for so far as this was necessary with a view to the question under investigation.

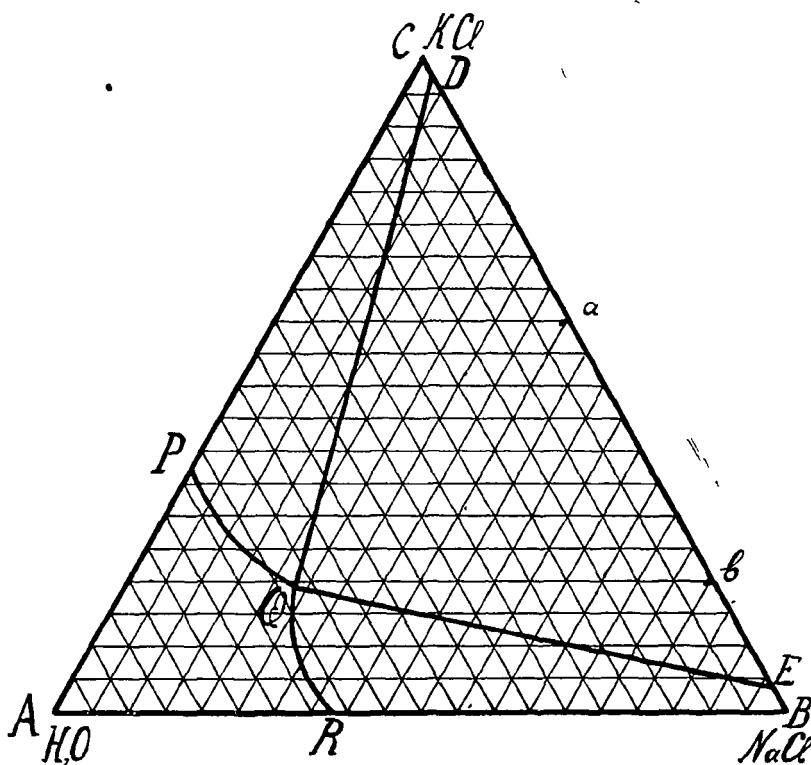


Fig. 2.

If no compound is found, and if D and E in Fig. 2 are the mixed crystal phases coexisting at 25° , we shall have to do with two solubility-isotherms PQ and QR , so that Q is the solution that coexists with the two solid phases D and E . If we start from two concentrations a and b , on the left-hand and the right-hand of the top Q , (see Fig. 1), it is clear that these two mixtures, which are homogeneous at temperatures above 407° , will consist of the two-phase complex $D + E$ at 25° , but in different ratio.

So when we shake these mixtures at 25° with such a quantity of water that the two solid phases continue to exist side by side, in *both* cases the coexisting solution will lie in Q , or in other words the coexisting solution will always possess the same concentration independent of the concentration of the phases.

If on the other hand we had to do with the appearance of a compound V (see Fig. 3), we should, working in the same way,

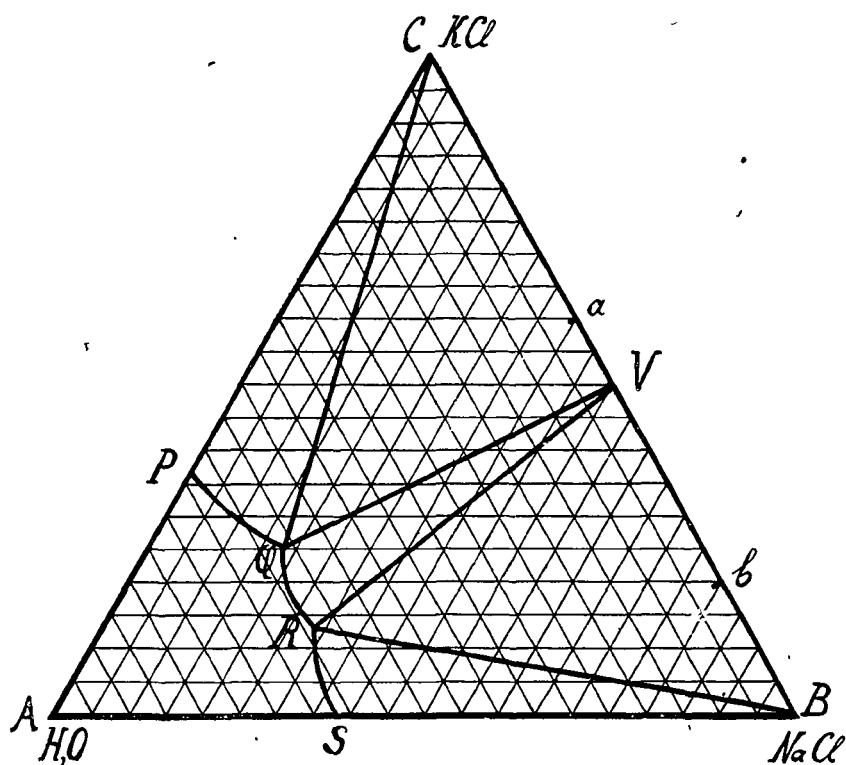


Fig. 3.

starting from the mixture a , obtain the coexistence of solid $\text{KCl} +$ solid compound $V +$ solution Q . Starting from b on the other hand we should get solid compound $V +$ solid $\text{NaCl} +$ solution R . So in this case the coexisting solution would *not* be the same for the two experiments.

3. The just-mentioned circumstances may, therefore, supply an exceedingly simple method to solve the pending question.

Two mixtures a and b of the substances which had been previously purified, were melted in a platinum crucible, after which they were

put in a vessel of Jena glass, which had been placed in a nitrate bath of $\pm 360^\circ$. The nitrate bath was then allowed to cool very slowly, in which the range of temperature between 370° — 340° was passed through in about 3 hours; the further cooling proceeded more rapidly. The obtained solid substance was then ground to powder, and then shaken in a thermostat with a little water at 25° for 2 hours, after which in the usual way a certain quantity of saturated solution was twice pipetted off.

We determined of each quantity obtained in this way:

1. the total weight.
2. the weight of the sum $\text{NaCl} + \text{KCl}$ (by careful evaporation, followed by heating to the temperature of melting).
3. the weight of KCl (according to SCHLÖSING-WENSE'S method).

At the same time for a comparison the solubility of the same mixtures *a* and *b* was determined at the same temperature, but when they had not been heated previously.

1	Mixture <i>a</i>		Mixture <i>b</i>	
	60% KCl	40% NaCl	20% KCl	80% NaCl
	Melted and slowly cooled down 2	Mixed mechanically at room temperature 3	Melted and slowly cooled down 4	Mixed mechanically at room temperature 5
KCl + NaCl (in gr. to 100 gr. solution)	31.59	31.61	31.63	31.56
	31.63	31.57	31.61	31.57
Weight KCl	11.01	11.00	11.04	11.01
	11.00	10.98	11.00	10.97
Weight NaCl	20.58	20.61	20.59	20.55
	20.63	20.59	20.61	20.60
Weight H ₂ O	68.41	68.39	68.37	68.44
	68.37	68.43	68.39	68.43

The weight of the *NaCl* has been calculated from the difference in weight between *KCl + NaCl* and *KCl*; the weight of the *water* has been calculated from the total weight of the solution, diminished by the weight of the $\text{NaCl} + \text{KCl}$.

The two mixtures *a* and *b* had the following concentration :

$$\begin{array}{l}
 a \left\{ \begin{array}{ll} 4,476 \text{ gr. KCl} & 60 \text{ mol. } \% \text{ KCl} \\ 2,340 \text{ gr. NaCl} & 40 \text{ mol. } \% \text{ NaCl} \end{array} \right. \text{ or} \\
 b \left\{ \begin{array}{ll} 1,492 \text{ gr. KCl} & 20 \text{ mol. } \% \text{ KCl} \\ 4,680 \text{ gr. NaCl} & 80 \text{ mol. } \% \text{ NaCl.} \end{array} \right.
 \end{array}$$

The result of the investigation is given in the preceding table, p. 561 in which all the quantities are calculated for 100 gr. of the mixture. It appears with the greatest clearness from the good agreement between the values in the columns 2, 3, 4, and 5 that in the two cases the coexisting liquid has the same concentration for the examined threephase equilibrium, from which follows that we have really to do here with the phenomenon of unmixing in the solid state, which, as is indicated in the *T,X*-figure, occurs over an ever diminishing region of concentration at higher temperature, terminating finally in an *upper critical mixing-point*.

Towards lower temperature the unmixing always increases so that

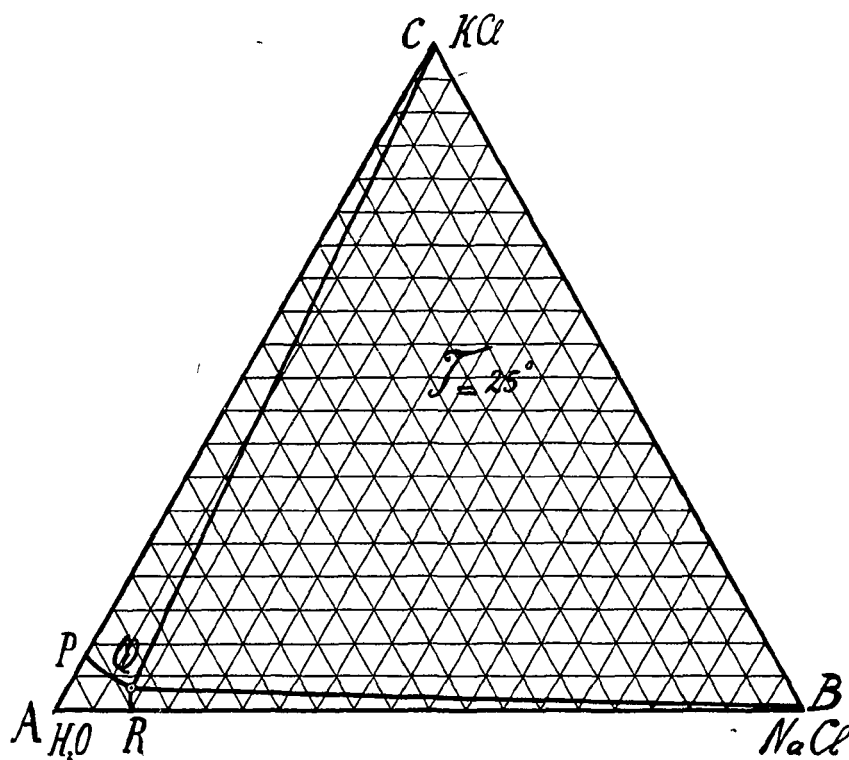


Fig. 4.

according to KRICKMEYER's investigations ¹⁾, only one of the two salts could be demonstrated in each of the coexisting solid phases at 25°.

The real situation of the isotherms at the temperature of 25° has been given in Fig. 4. According to this investigation the point *Q* lies at :

8,20 mol. % NaCl

3,43 „ „ KCl

88,37 „ „ H₂O

whereas VAN 'T HOFF and MEIJERHOFFER ²⁾ found

7,9 mol. % NaCl

3,5 „ „ KCl

88,6 „ „ H₂O.

The situation of the points *P* and *R* has not been determined anew, but was derived from the literature ³⁾.

P denoting the solubility of KCl at 25°, lies at 7,96 mol % KCl
and 92,04 „ „ H₂O

R denoting the solubility of NaCl at 25°, lies at 9,96 „ „ NaCl
and 90,04 „ „ H₂O.

4. What is remarkable about this is that these solubility-isotherms *PQ* and *RQ* must be connected continuously by means of a ridge with a partially metastable, partially unstable part, and that at the temperature of the upper critical mixing point this continuity enters the stable region.

In this connection it may be pointed out that by this investigation it has been proved for the first time that ζ -lines exist for solid mixtures, which must actually have a shape as is schematically given in Fig. 5. This line points to an interrupted series of mixed crystals, though the ζ -line is continuous. This continuity, however, lies here in the unstable region, and enters the stable region for the first time at the upper critical mixing point.

In Fig. 6 the *P, T*-projection of the system KCl—NaCl is schematically represented to show that here a plaitpoint curve for the solid substance ($S_1 = S_2$) must exist, which will probably run to infinite pressure.

In conclusion it may be stated that the phenomenon of the appearance of an upper critical mixing point in the solid state discussed here probably occurs for a number of other systems, as

¹⁾ Z. f. phys. Chem. 21, 53, (1896).

²⁾ Ber. Kgl. Pr. Akad. Wiss. Berlin 590 (1898).

³⁾ ANDREAÈ J. pr. Chem. 29, 456 (1889).

