

THE APPLICATION OF SIMULTANEOUS RECORDING
OF ELECTRICAL CONDUCTIVITY AND DTA IN THE STUDY
OF BINARY AND TERNARY SALT SYSTEMS

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(Received May 18, 1971)

The advantages of the simultaneous recording of electrical conductivity curve and DTA curves in the investigation of salt mixtures is demonstrated on a number of examples. With sufficiently slow recording, at a heating rate of 5–10°/min, all the changes occurring in the mixture investigated, and connected with the differing electrical conductivities of the different phases which appear and disappear in the process of heating or cooling, are well reflected on the electrical conductivity curve.

The application of DTA with the simultaneous recording of electrical conductivity variations was considered in the investigation of the phase diagrams of binary and ternary anhydrous salt systems. The electrical conductivity variation curve helps in the understanding of the nature of the phase transformations occurring during the heating and cooling of the substances investigated.

The electrical conductivity curves of certain substances have singularities by which these substances can be distinguished from similar compounds.

Thus, in the case of lithium, caesium and silver sulphates a large jump in the electrical conductivity (sharp rise of the electrical conductivity curve) is observed at the temperatures of the polymorphous transformations of these salts [1–3], in contrast to all other sulphates, where no such phenomenon is observed.

In the case of double salts, the electrical conductivity curves exhibit a great sensitivity to the presence of the least traces of the melt phase. Thus the recorded effects corresponding to the melting of the eutectic mixture or the solid solution, or compound formation can be distinguished from those of other phase transformations occurring in the solid state.

Results and discussion

Let us consider the curves of solidified sodium and silver sulphate melt mixtures. The phase diagram of a given system is characterized by the formation of a continuous series of solid solutions without a minimum for high-temperature α -modifications [4, 5]. The low-temperature β -modifications also form a continuous series of solid solutions with a minimum Ag_2SO_4 content of 40 mole% at 170°. High-temperature α -solid solutions have high electrical conductivity (partic-

ularly those containing over 40 mole% Ag_2SO_4) compared with β -solid solutions [1].

In Fig. 1 the endothermic effect at 190–230° corresponds to the transformation of the β -solid solution into the α -solution, no change being observed in the electrical conductivity curve. This means that the concentration and mobility of charge carriers in the α -solid solution at a given temperature are relatively small, its conductivity is insignificant and the electrical conductivity curve coincides with the base line. During further temperature increase, disorder (apparently of a cationic nature) develops, as a result of which the conductivity of the solid solution in-

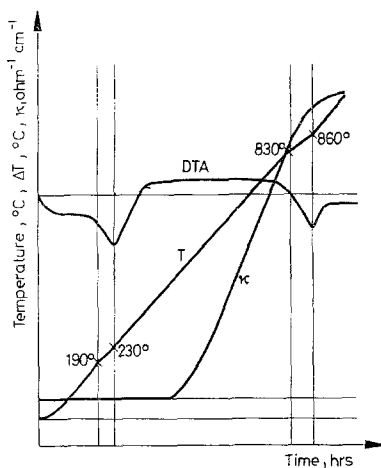


Fig. 1. Heating, DTA and electrical conductivity curves for a mixture of silver and sodium sulphates (80 mole% Na_2SO_4)

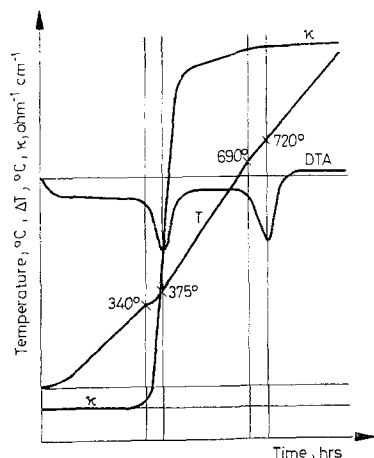


Fig. 2. Heating, DTA and electrical conductivity curves for a mixture of silver and sodium sulphates (20 mole% Na_2SO_4)

creases. The electrical conductivity curve is a rising line with an inflection at the melting point. The rate of conductivity increase decreases as soon as melting begins. This indicates that before melting the conductivity increase depended more on the increase of mobility of the charge carriers than on the rise in their concentration. During melting the mobility decreases while the concentration of mobile ions grows, as a result of which the slope of the electrical conductivity curve changes, but the conductivity continues to rise and reaches a maximum by the end of melting.

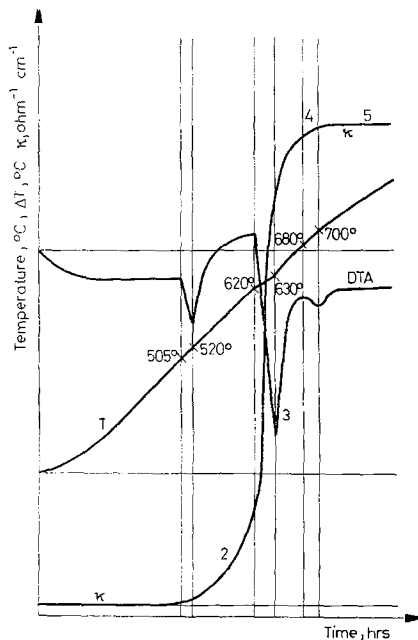


Fig. 3. Heating, DTA and electrical conductivity curves for a mixture of lithium and caesium sulphates (65 mole % Li_2SO_4)

The heating, DTA and electrical conductivity curves for mixtures containing excess silver sulphate have somewhat different forms. In Fig. 2 the endothermic effect at $340\text{--}375^\circ$ also corresponds to the transformation of the β -solid solution into the α -solid solution. This transformation, however, unlike the previous case, is accompanied by a sharp rise in electrical conductivity. Then, as the α -solid solution is heated, its conductivity gradually rises and reaches a maximum at the melting temperature of $690\text{--}720^\circ$.

The appearance of new phases in the system brings about a variation in the character of the temperature dependence of the conductivity, as a result of which inflections appear on the electrical conductivity curves. Individual curve sections characterize the various phases.

The curves of the equilibrium systems of the $\text{Li}_2\text{SO}_4 - \text{Cs}_2\text{SO}_4$ mixture furnish a good illustration of this. The phase diagram of this system is characterized by the presence of two maxima, corresponding to the incongruent melting of $\text{Cs}_2\text{SO}_4 \cdot 5\text{Li}_2\text{SO}_4$ at 640° , and of $\text{Cs}_2\text{SO}_4 \cdot \text{Li}_2\text{SO}_4$ at 730° [6, 7]. The modification transformations of individual salts and compounds are accompanied by sharp changes in electrical conductivity. For $\text{Cs}_2\text{SO}_4 \cdot \text{Li}_2\text{SO}_4$ this transformation occurs at 710° , and for $\text{Cs}_2\text{SO}_4 \cdot 5\text{Li}_2\text{SO}_4$ at 520° .

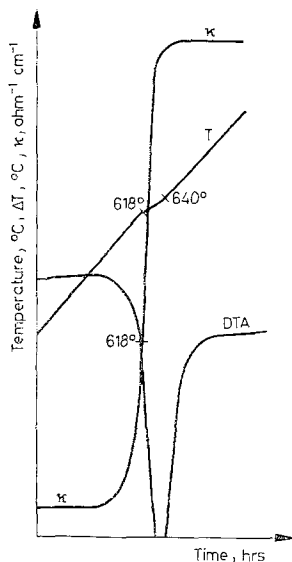


Fig. 4. Heating, DTA and electrical conductivity curves for a mixture containing 20 mole % Ag_2SO_4 , 10 mole % Li_2SO_4 and 70 mole % Cs_2SO_4

Fig. 3 shows the curve for the mixture of lithium and caesium sulphate containing 65 mole % lithium sulphate. Curve section 1 corresponds to the heating of $\text{Cs}_2\text{SO}_4 \cdot 5\text{Li}_2\text{SO}_4$. The conductivity of the compound changes only slightly, so that these changes are not recorded within the chosen scale. At 520° the transition of the non-conducting β -modification of $\text{Cs}_2\text{SO}_4 \cdot 5\text{Li}_2\text{SO}_4$ into the conducting α -modification is over. Section 2 corresponds to a change in the conductivity of this modification. At 620° eutectic melting begins, section 3 corresponding to the mixture of liquid and conducting solid phases. Section 4 corresponds to final melting, and section 5 to the liquid salt.

It was only natural that in triple salt systems the curve characterizing conductivity variations should clearly reflect phase transitions connected with the appearance of liquid (solidus system), conducting modifications, and chemical compounds.

On the examples of the ternary systems $\text{Li, Na, Ag} // \text{SO}_4$ and $\text{Li, Cs, Ag} // \text{SO}_4$,

it has been established that the electrical conductivity curves are similar to those of binary salt systems.

The melting of a ternary eutectic is characterized by an evenly and rapidly rising electrical conductivity curve.

Fig. 4 shows the curves for the heating of a salt mixture close to the ternary eutectic, containing 20 mole% Ag_2SO_4 , 10 mole% Li_2SO_4 and 70 mole% Cs_2SO_4 .

Eutectic melting starts at 618° and is accompanied by an increase of the electrical conductivity in discrete steps.

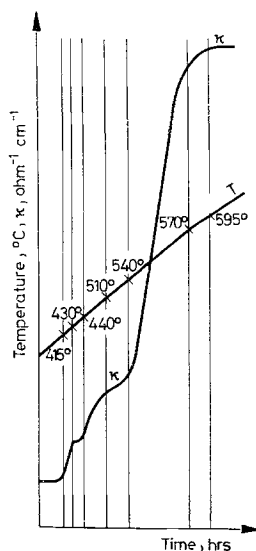


Fig. 5. Heating and electrical conductivity curves of a salt mixture containing 20 mole% Ag_2SO_4 , 50 mole% Li_2SO_4 and 30 mole% Cs_2SO_4

In view of the fact that the system contains an excess of Cs_2SO_4 compared with the true eutectic, the end of melting occurs at 640° . A change of slope appears on the temperature curve. The conductivity reaches its maximum at 640° .

In the curve of a mixture containing the same amount of silver sulphate (20 mole% Ag_2SO_4), but richer in lithium sulphate (50 mole%) than in caesium sulphate (30 mole%), one can observe thermal effects corresponding to the solid-phase transformations, each of which is distinguished by an inflection on the electrical conductivity curve (Fig. 5).

The differential curve is not shown in Fig. 5, so as not to confuse the figure. The curve demonstrates that in the equilibrium mixture a transition of the β -modification of $2\text{Li}_2\text{SO}_4 \cdot 3\text{Ag}_2\text{SO}_4$ to the α -form takes place at 415° , the decomposition of $2\text{Li}_2\text{SO}_4 \cdot 3\text{Ag}_2\text{SO}_4$ occurs at 430 – 440° , the transition of $\text{Cs}_2\text{SO}_4 \cdot 5\text{Li}_2\text{SO}_4$ to the α -form at 510° , and the transition of β - Li_2SO_4 to α - Li_2SO_4 at 546° . The melting of the ternary mixture begins at 570° , and ends at 595° .

This curve rises rapidly at the melting point of the ternary eutectic. However, even in this case the sections characterizing the appearance of a new phase are visible.

A slower heating or cooling of the mixture in question contributes to a better separation of the thermal effects and to the distinguishing of characteristic inflections on the electrical conductivity curve.

From a comparison of the slower cooling curves and the more rapid heating curves for the same substance, a difference is noted in the characters of the electrical conductivity curves. Fig. 7 shows the curve for an equilibrium mixture containing 30 mole % Ag_2SO_4 , 30 mole % Na_2SO_4 and 40 mole % Li_2SO_4 .

The following processes are reflected in the cooling curves: $635-625^\circ$ — solidification of α -solid ternary solutions, $520-455^\circ$ — transformation of α - Li_2SO_4 into β - Li_2SO_4 . Simultaneously the solid solution decomposes and forms the compound $\text{Na}_2\text{SO}_4 \cdot \text{Li}_2\text{SO}_4$. At 375° the formation of $2\text{Li}_2\text{SO}_4 \cdot 3\text{Ag}_2\text{SO}_4$ takes place. The endothermic peaks observed on the heating curves correspond to the decomposition of the compound $2\text{Li}_2\text{SO}_4 \cdot 3\text{Ag}_2\text{SO}_4$ at 375° , to the decomposition of the compound $\text{Na}_2\text{SO}_4 \cdot \text{Li}_2\text{SO}_4$ at $465-534^\circ$ and to the melting of the α -solid solution at $625-630^\circ$. Inflections are clearly visible on the electrical conductivity curve, corresponding to cooling on the appearance of each new phase in the mixture. These inflections are hardly noticeable on the electrical conductivity curve, in accordance with the more rapid heating.

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RÉSUMÉ — On montre à l'aide de plusieurs exemples relatifs à l'étude de mélanges de sels les avantages de l'enregistrement simultané de la conductivité électrique et de la courbe d'ATD. Pour une vitesse d'échauffement suffisamment lente, de 5 à $10^\circ/\text{mn}$, l'enregistrement de la conductivité électrique reflète tous les changements qui se produisent dans le mélange étudié et qui sont liés à une différence de conductivité électrique des différentes phases qui apparaissent et disparaissent au cours de l'échauffement ou du refroidissement.

ZUSAMMENFASSUNG — Die simultane Anwendung der Methoden der elektrischen Leitfähigkeitsmessung und der Differentialthermoanalyse ist sehr vorteilhaft für die Untersuchung von Salzmischen. Bei genügend langsamer Aufheizgeschwindigkeit (ca $5-10^\circ/\text{Min}$) werden alle Vorgänge, die während des Aufheizens und Abkühlens auftreten und mit verschiedener elektrischer Leitfähigkeit in den verschiedenen Phasen verbunden sind, in der Leitfähigkeitskurve widerspiegelt.

Резюме — На ряде примеров показана целесообразность применения одновременной записи электропроводности при исследовании солевых смесей. При достаточно медленной записи термограмм, со скоростью, примерно $5-10^\circ$ в минуту на кривой электропроводности четко фиксируются все изменения, происходящие в исследуемой смеси, связанные с различной проводимостью фаз, появляющихся и исчезающих в ней в процессе нагевания или охлаждения.