INVESTIGATION OF REACTIONS IN SOLIDS BY DTA

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(Received February 19, 1973)

Reactions in mixtures of solid alkali metal sulphates with barium chloride were investigated by DTA. The decisive role of an intermediate liquid was demonstrated.

It was established that the application of DTA with simultaneous recording of electrical conductivity in the investigation of the mechanism of interaction of mechanical non-equilibrium mixtures of anhydrous salts leads to data on the transitory existence of a labile eutectic, which to a certain extent affects the course of the reactions of the mixtures of solids.

One of the interesting and successful applications of DTA is for the investigation of reactions in mixtures of solids. DTA and simultaneous recording of electrical conductivity changes makes possible the establishment of the most essential stages in the solid-phase reactions and the role of some elementary stages involved in these complex heterogeneous processes. The use has revealed of DTA that in numerous reactions taking place in powdered mixtures of inorganic substances a decisive role is played by the formation of liquid or gaseous phases in the course of the process [1−4].

The present work gives some experimental data and a description of the exchange reactions in mixtures of solid anhydrous sulphates of alkali metals with barium chloride. The experimental procedure is described in detail in [5−9]. The heating rate was 10−12°/min, with sample weights up to 300 mg. All experiments were carried out with the heating cell described in [10]. X-ray phase analysis was used to identify the intermediates and reaction products.

Results and discussion

An exchange reaction between solid anhydrous salts is a complicated heterogeneous process, characterized both by purely solid-phase chemical transition within the reaction zone at the points of close contact between the particles of the reactants and by various physicochemical processes in which the formation of intermediate "non-solid" (liquid) phases is possible. The heating of the reactant mixture causes the excitation of all crystal lattice points of the substances taking part in the process. Such a state gives rise to a purely solid-phase reaction, occurring inhomogeneously throughout the volume and localized in space at certain

points. Due to diffusion inhibition this stage of the process proceeds at a com-
paratively low rate and as a rule is not indicated by DTA curves. With further
temperature rise the products formed in the first stage can form low-melting
eutectic mixtures with unreacted starting material.

Melting at the local centres, these mixtures give rise to the transition zone
throughout the reaction volume, and lead to the autocatalytic end of the process.
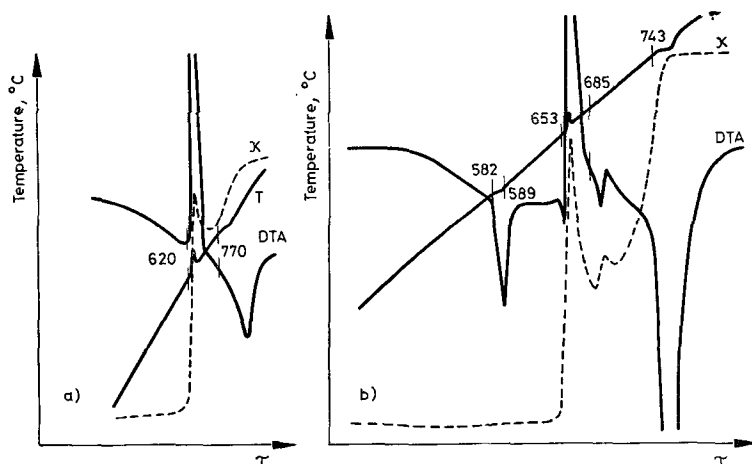

Fig. 1. Thermal curves of equimolecular mixture of barium chloride and a) sodium sulphate,
b) potassium sulphate

The above statements can be illustrated by the example of reaction between
barium chloride and sodium sulphate (Fig. 1a). It was shown earlier [1, 3] that in
the course of this reaction a decisive role is played by the formation of a liquid
phase (data obtained from investigation of the phase equilibrium Na, Ba // Cl, SO$_4$
[II] at 620°).

Thus, when determining the characteristics of reactions in the solid phase,
attention has to be paid to the interrelation between the solid and liquid phases,
and the possibility of formation of labile phases. This means that the answers to
the questions raised should be based on the main theoretical propositions of
physico-chemical analysis. To establish the nature of the intermediate phase ex-
perimentally and to determine their interrelation and interdependence we used
the "metastable diagonal method", which permitted the course of interphase
processes to be followed. The basis of the method is DTA investigation with
simultaneous recording of electrical conductivity changes of mixtures containing
the starting components in proportions corresponding to points on the metastable
diagonal. The data obtained for the reaction between sodium sulphate and barium
chloride are given in Fig. 2.

Thus the composition square includes the experimental data for the non-
equilibrium state and the phase diagram of the system Na, Ba//Cl, SO$_4$. The

latter, according to [11], is a simple eutectic system with two ternary eutectic points, $E_1 = 620°$ and $E_2 = 638°$. The use of the "metastable diagonal method" led to an interesting result: in whichever phase triangle (high temperature or low temperature) the $Na_2SO_4/BaCl_2$ mixture is located by its composition, the inter-action process begins at 620°, i.e. at the melting temperature of the eutectic with the lower melting point (full line, Fig. 2). Reheating (recooling of the metastable diagonal mixture gives the corresponding temperature points on the solidus lines (dotted lines, Fig. 2).
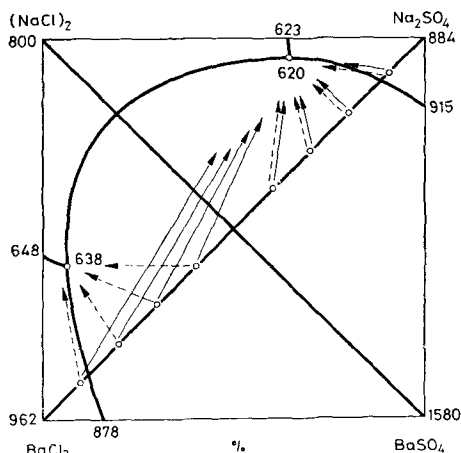

Fig. 2. Metastable diagonal method

It follows from the experimental data that in the reaction in question, irrespec-tively of the starting component ratio, the interaction process in the non-equi-librium mixture begins at a temperature which corresponds in the melting diagram to the melting temperature of the lower melting ternary eutectic.

However, such a correspondence is not observed in the reactions of $BaCl_2$ with K_2SO_4, Rb_2SO_4 or Cs_2SO_4. The interaction in these reactions starts at a temperature somewhat higher than the melting temperature of the lower melting ternary eutectic (see Tables 1 and 2).

Table 1

Reaction	Reaction temperature, °C	Eutectic melting temperature
$Li_2SO_4 + BaCl_2 = 2\,LiCl + BaSO_4$	465	464
$Na_2SO_4 + BaCl_2 = 2\,NaCl + BaSO_4$	620	620
$K_2SO_4 + BaCl_2 = 2\,KCl + BaSO_4$	653	640
$Rb_2SO_4 + BaCl_2 = 2\,RbCl + BaSO_4$	632	620
$Cs_2SO_4 + BaCl_2 = 2\,CsCl + BaSO_4$	556	549

Comparison of the data in Tables 1 and 2 shows the disparity to be observed for the phase diagram with the chemical compound. When a non-equilibrium mixture of potassium sulphate and barium chloride is heated initially at a comparatively low temperatures, the reaction $K_2SO_4 + BaCl_2 = 2KCl + BaSO_4$ is a purely solid-phase one. As soon as the temperature reaches 653° the reaction ends autocatalytically, simultaneously with a sharp rise of electrical conductivity (Fig. 1b), indicating the presence of liquid phase in the mixture.

Table 2

System	Eutectics		Equilibrium phases
Na,Ba // Cl,SO$_4$	E$_1$	620	Na$_2$SO$_4$, NaCl, BaSO$_4$
[11]	E$_2$	638	BaCl$_2$, NaCl, BaSO$_4$
K,Ba // Cl,SO$_4$	E$_1$	640	KCl, BaSO$_4$, 2 KCl · BaCl$_2$
[12]	E$_2$	654	BaCl$_2$, BaSO$_4$, 2 KCl · BaCl$_2$
	E$_3$	687	K$_2$SO$_4$, KCl, BaSO$_4$
Rb,Ba // Cl,SO$_4$	E$_1$	627	BaCl$_2$, BaSO$_4$, 2 RbCl · BaCl$_2$
[−X−]	E$_2$	620	RbCl, BaSO$_4$, 2 RbCl · BaCl$_2$
	E$_3$	630	Rb$_2$SO$_4$, RbCl, BaSO$_4$
Cs,Ba // Cl,SO$_4$	E$_1$	549	CsCl, BaSO$_4$, 2 CsCl · BaCl$_2$
[−X−]	E$_2$	572	Cs$_2$SO$_4$, BaSO$_4$, CsCl
	E$_3$	579	BaSO$_4$, 2 CsCl · BaCl$_2$, CsCl · BaCl$_2$
	P	589	BaCl$_2$, BaSO$_4$, CsCl · BaCl$_2$

[−X−] Systems studied by the authors of the present work.

Hence, in a non-equilibrium mixture of potassium sulphate with barium chloride the chemical reactions does not begin at the temperature at which melting of the low-melting eutectic (640°) is already possible. This means that in the solid-phase stage of the process direct chemical interaction results in interchange products only and no double salt $2KCl · BaCl_2$ is formed; otherwise, the presence of the latter would affect the temperature of the beginning of noticeable interaction markedly, since the ternary eutectic of the compound $2KCl · BaCl_2$ and the components melts at 640°.

The same regularity is observed in the reaction between barium chloride and caesium sulphate (Fig. 3b; Tables 1, 2).

Of great importance is the fact that the interaction between rubidium sulphate and barium chloride (Fig. 3a) begins at 632°, which corresponds to the melting point of the eutectic composed of the components Rb_2SO_4, RbCl and $BaSO_4$. This confirms the above conclusions and shows that also in the case when the reactants and products of the reaction in phase equilibrium produce a complex morphology diagram of melting, the interaction process is connected with the formation of a liquid phase. In this case the elements M_2SO_4, MCl, $BaCl_2$ and $BaSO_4$ are the only components of the reacting mixture and no double salts are involved.

The equilibrium systems K, Ba//Cl, SO_4 and Cs, Ba//Cl, SO_4 have ternary eutectic points $E = 587°$ and $E = 572°$, respectively. It follows from the DTA (Figs 1 and 3b) that the reactions of non-equilibrium mixtures begin at temperatures lower than these and involve the formation of a liquid phase. The above results indicate that under the present conditions a liquid phase can be formed only by melting of a labile eutectic. Indeed, if the system K, Ba//Cl, SO_4 (Cs, Ba//Cl, SO_4) were an ordinary eutectic system, then its second ternary eutectic would consists of KCl, $BaCl_2$ and $BaSO_4$ (CsCl, $BaCl_2$, $BaSO_4$) with melting point below 687° (572°) due to the replacement of K_2SO_4 (or Cs_2SO_4) by $BaCl_2$.
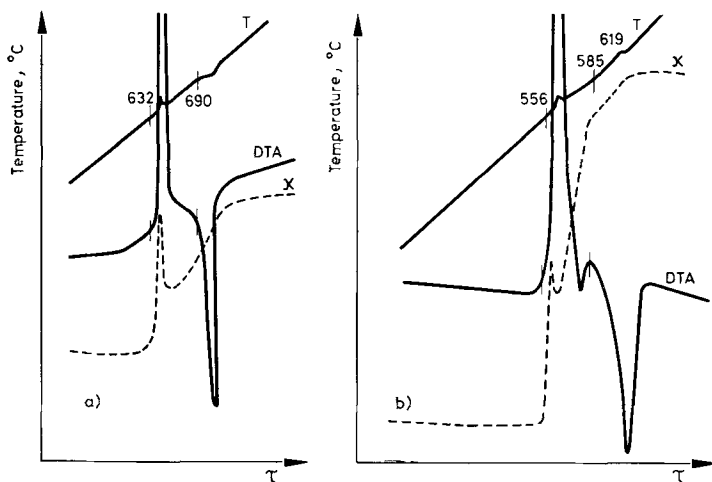

Fig. 3. Thermal curves of equimolecular mixture of barium chloride and a) rubidium sulphate, b) caesium sulphate

It is well known that the presence of unstable phases is observed in solid-phase transitions, and the real chemical process is always accompanied by a deviation of the system from the equilibrium state. The literature describes an example of a solid-phase reaction, in the mechanism of which the presence of a labile eutectic plays a decisive role [3, 5]. The melting point of a labile eutectic in the investigated reactions is somewhat higher than that of the eutectic with the lower melting point in the corresponding system M^I, M^{II}//Cl, SO_4. To substantiate this, we used the known linear liquids line principle [13] and also many experimental results concerning binary halide systems. The melting temperature of a labile eutectic depends on the melting temperature of a chemical compound formed in the system. At first sight this seems to be an insoluble contradiction, since a labile eutectic can be formed only in the non-equilibrium state when these chemical compounds are absent. However, the question here is the observable melting

temperature of a labile eutectic. In fact, this temperature can be above or below the melting temperature of the eutectic with the lower melting point (Fig. 4) since the positions of the stable parts aE_1D and bE_2D in the equilibrium systems obtained are determined by the melting temperature of the chemical compound. The present examples describe the first of possible types of labile eutectic formation.
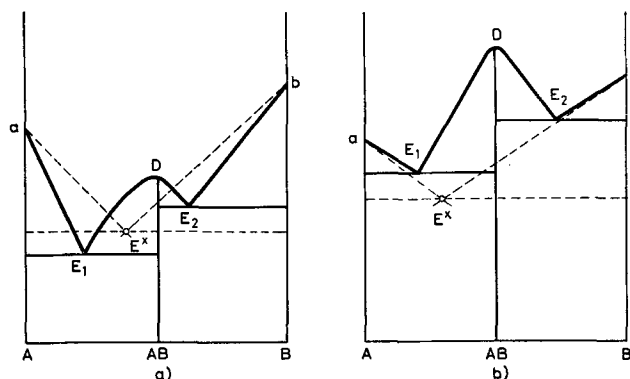

Fig. 4. Schematic diagram for determination of the possible melting temperature of labile eutectic

Comparison of data obtained from investigation of non-equilibrium mixtures by the metastable diagonal method, numerous experimental data on binary and multi-component system and also the examination of theoretical aspects of physico-chemical analysis lead to the conclusion that the reactions of barium chloride with potassium and caesium sulphates occur at a perceptible rate due to the presence of a liquid phase, which results from labile eutectic melting.

Hence a determining role in "fast" solid-phase reactions between barium chloride and alkali metal sulphates is played by the formation of low-melting mixtures, which can be either an eutectic or, depending on the properties of the reactants, a labile phase. The formation of the labile state is possible in the chemical reactions occurring under the conditions far from those of equilibrium. It is known that such phenomena can strongly affect the mechanism of formation of a new phase. Apparently, in the reverse cases, i.e. when an unstable phase is consumed (the examples considered here), such phenomena can play a substantial role. In all probability, therefore, the labile eutectic can be considered not only as a phase which when melting provides a close contact between the reactants, but also as a specific intermediate active state. This can explain the sufficiently high-speed DTA recordings in the processes investigated.

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RÉSUMÉ — On a suivi par ATD la réaction de mélanges de sulfates de métaux alcalins, à l'état solide, avec le chlorure de baryum et montré le rôle décisif d'une phase liquide intermédiaire.

L'emploi de l'ATD conjugué avec l'enregistrement simultané de la conductivité électrique a permis d'obtenir des données sur l'existence transitoire d'un eutectique labile, qui, dans une certaine mesure, peut jouer un rôle sur les réactions des mélanges de composés solides.

ZUSAMMENFASSUNG — Die Reaktion in den Mischungen fester Alkalimetallsulfate mit Bariumchlorid wurde an Hand der DTA studiert. Die entscheidende Rolle der intermediären Flüssigkeit in den geprüften Reaktionen wurde bewiesen.

Es wurde festgestellt, daß die Anwendung der DTA bei gleichzeitiger Registrierung der elektrischen Leitfähigkeit bei dem Studium des Wirkungsmechanismus mechanischer Nicht-Gleichgewichtsmischungen nichtwäßriger Salze Angaben bezüglich eines labilen Eutektikums kurzer Lebensdauer ermöglicht, welches in gewissem Maße den Verlauf der Reaktionen von Festkörpermischungen beeinflußt.

Резюме — Методом ДТА исследованы реакции в смесях твердых сульфатов щелочных металлов с хлоридом бария. Показана решающая роль промежуточных жидких фаз в изученных реакциях. Установлено, что изучая методом ДТА с одновременной записью электропроводности механизм взаимодействия в механических, неравновесных смесях безводных солей, можно получить данные о существовании в течение короткого промежутка времени лабильной эвтектики, оказывающей определенное влияние на ход реакции в смесях твердых веществ.