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INVESTIGATION OF EXCHANGE REACTIONS BETWEEN ALKALINE EARTH METAL OXIDES AND SOME TRANSITION METAL HALIDES

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DTA and the simultaneous recording of electrical conductivity were applied for the investigation of exchange reactions between alkaline earth metal oxides and some lead, copper and nickel halides. Although the possibility of the gaseous phase is not excluded for the majority of the reactions investigated, it is either the appearance of a liquid phase or the polymorphous transformation of CaO that has the decisive effect on the interaction mechanism.

Reactions of the alkaline earth metal oxides have been repeatedly studied, but at present there is no common view as to their mechanisms. The theory of Hedvall [1] and Tamman [2] explained such reactions solely on the basis of the extreme reactivity of the alkaline earth metal oxides and claimed them to be strictly solid-phase reactions. According to Hedvall [3] the reactions between alkaline earth metal oxides and various salts mostly start at a characteristic temperature for each individual oxide

Substance	T°
BaO	345
SrO	455
CaO	530

This phenomenon of the constancy of the temperature at which one reagent begins to interact with others is referred to as the Hedvall effect. Since the alkaline earth metal oxides are strongly hygroscopic, this constancy of the temperature at which interaction starts led some investigators to suggest that Hedvall and Tamman had used hydroxide-contaminated oxides whose melting points were rather low, and the interaction had been brought about by the presence of a liquid phase [4, 5]. A number of attempts were made [6 – 8] to reproduce the Hedvall effect. Some of these ended in failure, as was the case with calcium and magnesium oxides for instance [8]. In the case of barium and strontium oxides the Hedvall effect was reproduced only when the experiment was carried out in air.

However, none of the above works made the point of demonstrating the appearance of a liquid phase at the moment of interaction.

In this paper the appearance of a liquid phase is investigated and its effect on the interaction mechanism is discussed.

The proof of the existence of a liquid phase became possible only after the electrical conductivities of mixtures of solid substances were recorded together with the heating curves [9].

Certain transition metal halides were chosen as the second reagents.

As regards the crystallographic changes undergone by some of the chosen reagents during heating, it was wished to ascertain their effects on the start of the exchange reaction. According to Hedvall, the reactivity of the solid phase increases at a temperature close to that of the phase transformation.

It was further wished to elucidate the effect of the gaseous phase on the reaction in question.

Experimental

The investigation of reactions in the solid mixtures was carried out by DTA and by the simultaneous recording of the electrical conductivity. This method proved to be very sensitive to the appearance of the slightest traces of a liquid phase. DTA curves and electrical conductivity changes were recorded using a Curnakov pyrometer (PC-52). A Pt/Pt-Rh thermocouple was used. Calcined alumina was employed as reference material. The reactions were investigated in air. Reactant mixtures were placed in a narrow (5 mm diameter), 50 mm long quartz test tube. The thermocouple was inserted into the sample, the distance between the ceramic tube of the thermocouple (4 mm diameter) and the walls of the test tube being very small. An X-ray analysis of samples of the reagent mixtures heated to different temperatures was also carried out.

The starting BaO and SrO were prepared from $Ba(NO_3)_2$ [10] and $SrCO_3$ [11], respectively. CaO is an analytically pure reagent. Before use the oxides were calcined at a temperature between 1000 and 1200° for 6 hours. CuBr was produced by a known method [10]. Chemically pure $PbBr_2$ was recrystallized three times, dried and remelted. $NiCl_2$ was produced by dehydrating $NiCl_2 \cdot 6H_2O$ [12].

The reactions were carried out with the starting reagents in equimolecular proportions.

To date we have studied reactions between barium oxide and copper chlorides, lead and copper bromides and copper iodides; between calcium oxide and lead, copper and nickel chlorides, bromides and iodides; between strontium oxide and nickel chloride, bromide and iodide. The DTA curves and electrical conductivity vs. temperature curves for several reactions are presented in Figs 1–4.

Investigation of the reaction between BaO and CuBr

The interaction is exothermic at 360° (Fig. 1) and is accompanied by an increase in the electrical conductivity, i.e. the interaction proceeds through a liquid phase. After the exothermic peak the electrical conductivity falls since solid reaction products appear. On the further increase of temperature, the electrical conductivity again increases, due to the melting of the reaction product $BaBr_2$ at 730° in the presence of unreacted starting reagents and the second product, Cu_2O.

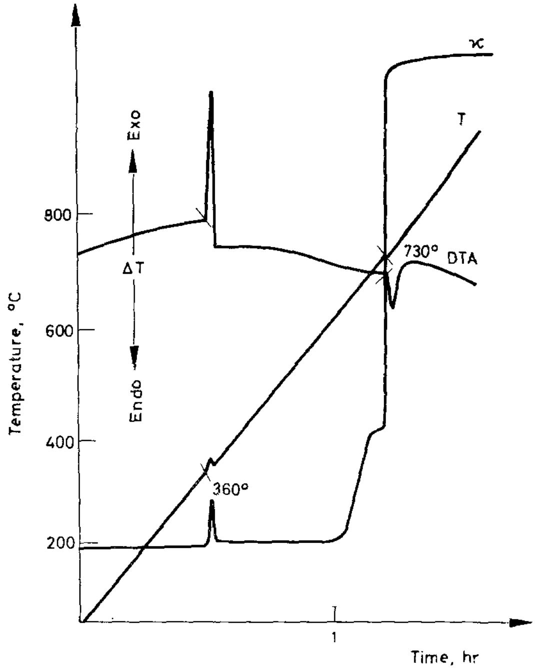

Fig. 1. DTA and electrical conductivity curves for a mixture of BaO and CuBr

The appearance of the liquid phase at 360° is due to the melting of the $Ba(OH)_2$–BaO eutectic [4, 7]. According to the available data [13] the $Ba(OH)_2$–$BaBr_2$ eutectic melts at 345°. The appearance of the liquid phase exerts no decisive effect on the reaction rate since it improves the contact between the solid reagent grains, whereas the melting of the BaO–$Ba(OH)_2$ eutectic results in the transition of one of the initial reagents to a liquid phase and the reaction proceeds between the solid CuBr and liquid BaO.

Investigation of the reaction between BaO and $PbBr_2$

A sharp exothermic peak is observed at 360° on the DTA curve of the powdered mixture of $PbBr_2$ and BaO (Fig. 2), which shows the reaction between the initial components. A maximum on the electrical conductivity curve corresponds to the exothermic peak on the DTA curve. This indicates the appearance of a liquid phase. Thus, an instantaneous exchange reaction occurs between $PbBr_2$ and BaO with the participation of a liquid phase, apparently the molten eutectic BaO–BaO–$Ba(OH)_2$.

The reaction mechanism can be described as follows:

1. The formation of a liquid eutectic:

$$[BaO]_s + [Ba(OH)_2]_s \rightarrow [BaO + Ba(OH)_2]_l$$

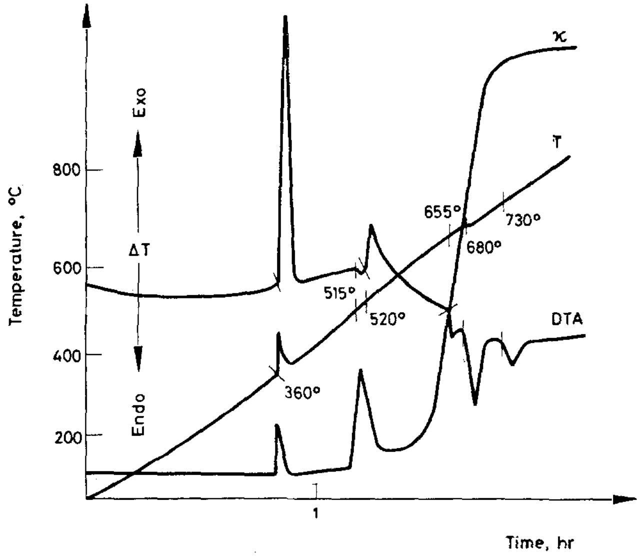

Fig. 2. DTA and electrical conductivity curves for a mixture of BaO and $PbBr_2$

2. The reaction between liquid barium oxide and solid lead bromide: $[BaO]_l +$ $+ [PbBr_2]_s \rightarrow [BaBr_2]_s + [PbO]_s$, and the reaction between liquid barium hydroxide and solid lead bromide:

$$[Ba(OH)_2]_l + [PbBr_2]_s \rightarrow [BaBr_2]_s + [PbO]_s + [H_2O]_g$$

3. At 370° $PbBr_2$ melts and the reaction between the components proceeds in the molten phase:

$$[BaO]_l + [PbBr_2]_l \rightarrow [BaBr_2]_s + [PbO]_s$$

4. After the liquid eutectic is passed, the reaction mechanism can be described by the equation:

$$[PbBr_2]_l + [BaO]_s \rightarrow [PbO]_s + [BaBr_2]_s$$

As a result of the reaction solid products are formed, and therefore the electrical conductivity returns to zero. It again increases at about 500°. Near this temperature (515°) the endothermic melting effect is observed. Apparently this is the melting of the solid solution of $BaBr_2$ with the unreacted $PbBr_2$. The reaction takes place in the presence of the liquid phase, which is reflected on the curve by a small exothermic effect at 520°. After the second stage of the reaction (520°) the system contains a certain amount of $BaBr_2$. In order to melt $BaBr_2$ with $PbBr_2$ present it is sufficient to heat the mixture up to 655°. This can be seen on the DTA curve. The newly formed liquid phase causes the reaction, which is not indicated by the DTA curve due to the low reaction rate. The reaction results in an increase of the amount of $BaBr_2$ in the system, and a new endothermic effect of $BaBr_2$ melting in the presence of $PbBr_2$ is observed at 680°. As the temperature rises to 730°, PbO melts in the presence of the salts $PbBr_2$ and $BaBr_2$.

Investigation of the reaction between SrO and $NiCl_2$

On the heating curve (Fig. 3) for a mixture of strontium oxide and nickel chloride 5 exothermic effects are observed at 240, 290, 420, 450 and 490°. No increase of the electrical conductivity occurs at these temperatures, and thus the conclusion can be drawn that the exchange reactions take place without the participation of a liquid phase. The following experiment was performed to elucidate the role of the gaseous phase. Strontium oxide was placed over the halide, and the thermocouple and the electrodes were introduced only into the strontium oxide. In this case an exothermic interaction was observed at 300° on the DTA curve. X-ray analysis showed that NiO and $SrCl_2$ were produced in the reaction.

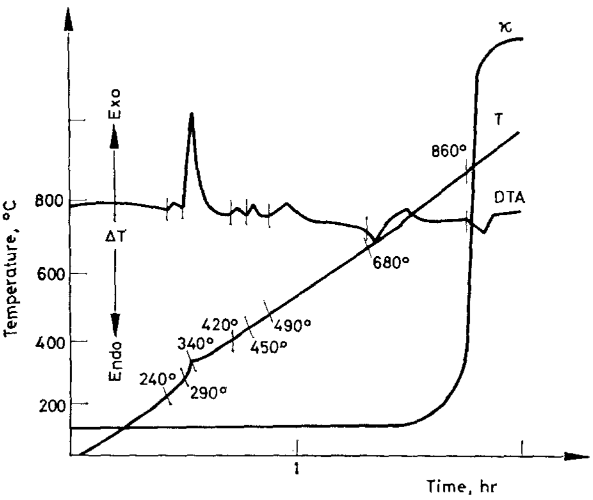

Fig. 3. DTA and electrical conductivity curves for a mixture of SrO and $NiCl_2$

On the basis of the available data the following mechanism can be suggested for the interaction of NiO and $SrCl_2$. On heating, the exchange reaction begins at 240°, and at 300° when there is no direct contact, as a result of the appearance of the first portions of gaseous $NiCl_2$ on the surface of SrO grains the reaction proceeds. This stage corresponds to the activation period due to the formation of "quasi-molecules" and molecular surface films. Afterwards, however, the reaction slows down, since the resulting solid products cover the SrO particles and thus hinder the penetration of the molecules of gaseous $NiCl_2$ (the presence of $NiCl_2$ in the SrO layer in the absence of direct contact between the reagents is detected by X-ray phase analysis), i.e. a kind of disactivation of the molecular films occurs. After the surface of the strontium oxide grains has been covered by solid reaction products and the surface reaction is over, diffusion increasing with temperature becomes a predominating process. Thus the second stage of the reaction at 290° proceeds with the participation of $NiCl_2$ molecules which diffuse through the reaction product layer towards the SrO particles and whose mobility increases with temperature. Then the reaction slows down again, since only a limited number of $NiCl_2$ molecules succeed in diffusing through the thickening reaction product layer at this temperature. However, as soon as the gaseous $NiCl_2$ molecules diffuse through the newly-formed reaction product layer towards the SrO crystalline lattice, which is also promoted by temperature increase, the reaction resumes at 420°, and then again becomes slower due to the formation of a new reaction product layer on the surface of the SrO grains. The rate of reaction, which is determined by the rate of diffusion, increases with temperature. The amount of gaseous $NiCl_2$ and the mobility of its molecules also increase, and so

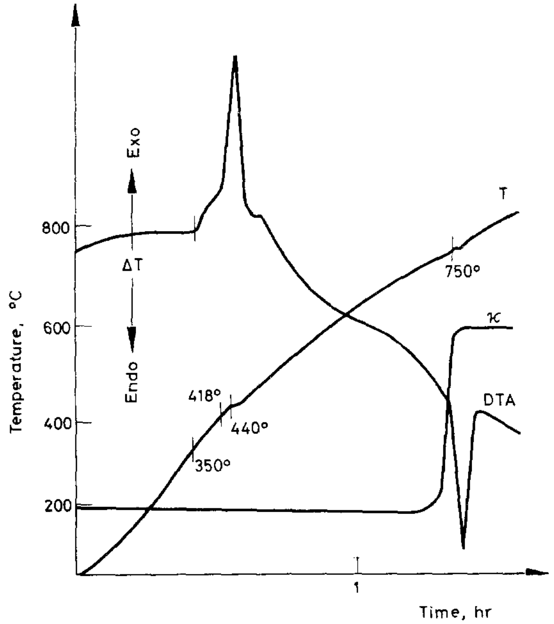

Fig. 4. DTA and electrical conductivity curves for a mixture of CaO and $NiCl_2$

the reaction is resumed at 450°. The exothermic peak at 490° is apparently linked with the enlargement of the crystals of the newly-formed compound. The endothermic effects at 680° and 860° are the results of phase transition and melting of $SrCl_2$ [14], respectively.

Investigation of the reaction between CaO and $NiCl_2$

A large exothermic peak due to reagent interaction is observed at 418 – 440° on the DTA curve (Fig. 4). The electrical conductivity does not change in the process. The high reaction rate is favoured by the polymorphous transformation of calcium oxide which occurs at 440° [15]. However, judging from the DTA curve the interaction already begins at 350°. The heating curves recorded when there was no direct contact between the reagents showed that the reaction took place n the gas phase. The endothermic peak at 750° indicates the melting of $CaCl_2$ [14].

Conclusions

1. The reactions detected on the DTA curve as an exothermic peak proceed either with the participation of a liquid or a gaseous phase, or are due to polymorphous transformations.
2. The liquid phase appearing in the reaction mixture and causing reaction between the solid substances may be either a binary oxide-hydroxide or reagent-product eutectic, or a ternary eutectic formed by the reaction products and one reagent, or may be due to the melting of the reagent-product solid solution.
3. There are instances of chemical interaction not accompanied by an increase in electrical conductivity and proceeding either through the gaseous phase, formed by the volatilization of the halides, or due to the polymorphous transformation of calcium oxide.

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Résumé — Emploi simultané de l'ATD et de la mesure de la conductivité électrique pour étudier les réactions d'échange entre les oxydes des métaux alcalino-terreux et différents halogénures de plomb, cuivre et nickel. Bien que la possibilité d'une phase gazeuse ne soit pas exclue pour la majorité des réactions étudiées, l'effet décisif sur le mécanisme d'interaction est provoqué par la fusion ou par la transformation polymorphique de CaO.

Zusammenfassung — Differentialthermoanalyse und elektrische Leitfähigkeitsmessungen wurden gleichzeitig zur Untersuchung der Austauschreaktionen zwischen Alkalierdoxyden und Blei-, Kupfer- und Nickelhalogeniden angewandt. Obwohl die Möglichkeit einer Gasphase für die meisten dieser Reaktionen nicht ausgeschlossen werden kann, ist entweder die Schmelze oder die polymorphe Umwandlung des CaO entscheidend für den Interaktionsmechanismus verantwortlich.

Резюме — Методом ДТА и одновременной регистрации электропроводности пересмотрены реакции взаимодействия оксидов щелочноземельных металлов с некоторыми галогенидами свинца, меди и никеля. Хотя возможность газофазовой ступени и не исключена для большинства изученных нами реакций, решающее влияние на механизм взаимодействия оказывают либо появление расплава, либо полиморфное превращение CaO.