Interaction of hygroscopic halides with reactive gas atmosphere at elevated temperatures

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The causes resulting in contamination of ionic halides with oxygen-containing admixtures at elevated temperatures and factors affecting the hydrolysis of those salts have been considered. The interaction of molten hygroscopic ionic halides with halogenating agents has been examined and main regularities of those processes have been considered.

Проведен анализ причин, приводящих к загрязнению ионных галогенидов (щелочных, щелочноземельных и редкоземельных элементов) кислородсодержащими примесями при высоких температурах, и факторов, влияющих на процессы гидролиза указанных солей. Рассмотрены процессы взаимодействия расплавов гигроскопичных ионных галогенидов с галогенирующими агентами и проанализированы основные закономерности их протекания.

The manufacturing of special purity grade halides of I–III Group metals and rare-earth elements and the growing of single crystals from the compounds mentioned are accompanied by interaction of the halides with oxygen-containing components of the gas medium as well as with water contained both in the gas medium and in the raw materials. Although it is possible to minimize the effects of gas medium and free water in the raw mixture, it cannot avert the hydrolysis processes at elevated temperatures that result in the material contamination with oxygen-containing impurities. The high-temperature hydrolysis processes in hygroscopic halides became of a special importance in connection with the wide use of lanthanide halides as matrices of fast-acting scintillators.
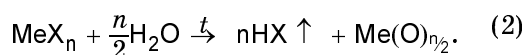
The removal of oxygen-containing impurities from alkali halides (mainly of NaI:Tl and CsI:Tl) was simple enough. The main aspects of the purification processes using various halogenating agents are described in detail in [1–4]. Those aspects were extended a priori over essentially all halides being in use at that time, so there were no reasons for reconsideration, e.g., of the work [5]. During the last few years, novel scintillation materials are under active development based on lanthanum chloride and bromide activated with cerium [6, 7] exceeding considerably NaI:Tl in the performance parameters. These materials, as well as some similar ones, are, however, very hygroscopic, thus causing difficulties in the raw material preparation, the crystal growth and treatment. The current drying techniques, e.g., of sodium iodide, are inefficient. The vacuum drying, even when carried out at a cautious temperature elevation, results in carbon formation in the raw mixture and appearance of oxygen-containing impurities.

In this work, the processes are considered resulting both in formation of oxygen-containing impurities in ionic halides at ele-

vated temperatures and in removal of those impurities. The former include pyrohydrolysis affecting negatively the final product quality, while the latter, treatment of halide melts with various halogenating agents favoring the improved performance characteristics of the halide materials.

The pyrohydrolysis of ionic halides results in a partial or complete decomposition under formation of the corresponding hydrogen halide and the metal oxide (hydroxide):

$$MeX_n + nH_2O \overset{t}{\rightarrow} nHX \uparrow + Me(OH)_n \quad (1)$$

$$MeX_n + \frac{n}{2}H_2O \overset{t}{\rightarrow} nHX \uparrow + Me(O)_{n/2}. \quad (2)$$

The most of well-known works associated with determination of thermodynamic or kinetic parameters of halide or melted halide reactions with water vapor at elevated temperatures are aimed just at pyrohydrolysis [8–10]. There are several causes of the water appearance in the atmosphere above a crystalline halide under heating:

— the water presence in raw mixture due to insufficient drying or to dry material contact with atmosphere;

— a high residual pressure at the vacuum drying;

— decomposition of oxygen-containing organic impurities.

The first cause requires no comments. The second one is obvious enough, too: the higher the residual pressure is, the higher is the decomposition temperature of the halide crystal hydrate, so the last fraction of water passing through the anhydrous halide heated up to a higher temperature cause its hydrolysis. This process is also favored by inhomogeneous heating of the bulky material, due to the fact that its outer layers have a higher temperature than the inner ones. The influence of such processes can be reduced to a great extent by using technologies providing a homogeneous heating of the whole raw material volume, e.g., drying using microwave heating.

The third cause is not so obvious, and its influence intensity is connected with the raw material purity and its pre-history. If the raw mixture contains nonvolatile oxygen-containing organic impurities, those will decompose at a certain temperature according to the following general scheme:

$$C,H,O \rightarrow \quad (3)$$
$$\rightarrow C \downarrow + C_nH_m \uparrow + CO_2(CO) \uparrow + H_2O \uparrow ,$$
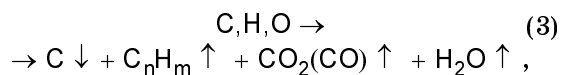
where (C,H,O) is a general designation of an oxygen-containing organic substance. This process is manifested itself usually as the raw material darkening (due to release of carbon), the darkening extent depending on the organic impurity content. The water released interacts with the halide. If CO_2 is present in the gas atmosphere above the mixture, the oxide or hydroxide being formed is subjected to simultaneous carbonization resulting in the corresponding carbonate. In the case of alkali or alkali-earth halides, the carbonate is stable enough up to rather high temperatures (about 1000 K); as to rare-earth halides, the carbonate is decomposed at about 700 K, i.e., prior to the base material melting. Thus, the halide raw material becomes contaminated with oxo compounds during the drying mainly due to the presence of oxygen-containing organic impurities but not due to the process regime.

The halide hydrolysis process at high temperatures can be presented as

$$H_2O \uparrow + 2X^- \rightarrow 2HX \uparrow + O^{2-}, K_{(4)}, \quad (4)$$
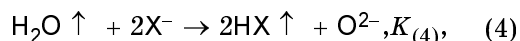
where X^-, HX is the general designation for halide ion (including the constitutional one, e.g., in solid NaCl) and hydrogen halide, respectively; O^{2-}, the general designation for oxide ion (including the constitutional one, e.g., in solid LaOCl, BaO). The extent of the process (4) shift from left to right depends on several factors, mainly on temperature, the halide acidity (i.e., the bond strength between the halide cationic base and the oxide ions) and the corresponding hydrogen halide stability at the specified temperature. The acidity of a material is defines as its ability to bind cations, oxide ions in the case of question; it depends on the material cationic composition, the corresponding process can be presented as

$$Me^{n+} + \frac{n}{2}O^{2-} \rightarrow MeO_{n/2}, \quad (5)$$

where Me^{n+} is the general designation for the halide-forming metal cation. Since the oxide ion does not exist in isolated form, the substance acidity is a relative characteristic. For example, the cation in melted salts is considered as an acidic one, when the equilibrium constant for (5) in eutectic KCl–NaCl or CsCl–KCl–NaCl melts exceeds 1,

that is, the acidity is determined with respect to Na^+ ions being the most acidic cation in the mentioned melts [11].

Here are two known methods to estimate the melt acidity. The first one is based on determination of the hydrolysis constant ($pK_{(4)}$) of the system under study and its comparison with the corresponding value for KCl–NaCl melt ($pK_{(4)} \sim 14$), that is used as a reference. The function

$$\Omega = 14 + \lg(p_{HCl}^2 / p_{H_2O}) = 14 - pK_{(4)} \quad (6)$$

is used as the acidity parameter. Here, p_{HCl} and p_{H_2O} are partial pressures of HCl and H_2O in the gas mixture, respectively. The function (6) shows the number of decimal orders by which the acidity of a specific melt exceeds that of the equimolar KCl–NaCl mixture (where $\Omega = 0$). It was supposed that the function (6) will make it possible to estimate the equilibrium constant changes when passing from one melt to another, but the supposition was not confirmed in practice. Another approach consists in determination of the equilibrium constants for indicator "acid/base" couples in the melt under consideration (pK_L) and in the KCl–NaCl melt ($pK_{KCl-NaCl}$). The difference of those constants is referred to as the oxo-basicity index (pI_L) of the melt L being studied:

$$pI_L = pK_L - pK_{KCl-NaCl}. \quad (7)$$

This parameter is similar to Ω in its physical sense. The parameters obtained using that method forecast well enough the change of equilibrium constants when passing from one melt to another, except for reaction (4).

The acidity indices of melted media, pI_L and Ω (or $pK_{(4)}$) are in correlation (Fig. 1). It is to note, however, that the change of equilibrium constants for (4) when passing from one melt to another exceeds considerably the difference between the corresponding acidity indices. Perhaps that deviation is caused by the fact that the most acidic melts are simultaneously the most hygroscopic ones. In this case, the water solubility in those melts exceeds considerably the values predicted by the Henry law. The melt contents an appreciable amount of water that could result in formation of H_3O^+ ions that intensify significantly the system acidic properties. Thus, in the studied mentioned, the equilibrium (4) is not only an
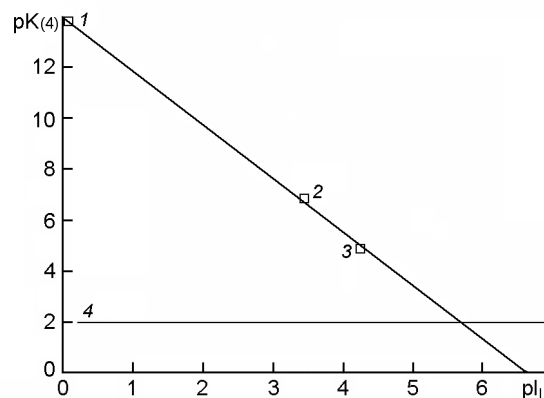

Fig. 1. Dependence of $pK_{(4)}$ on the basicity index pI_L for eutectic melts KCl–NaCl (*1*), KCl–LiCl (*2*), KCl–CaCl$_2$ (*3*) at 1000 K.

indicator reaction but also a way to increase the acidity of a hygroscopic melt.

It follows from Fig. 1 that as the acidity of a melted halide system increases, its trend to hydrolysis becomes intensified. So, KCl, NaCl, and CsCl ($pK_{(4)} \sim 14$, $pI_L \sim 0$) are not hydrolyzed essentially under heating and melting, and a substance having acidic properties was to be added to those materials when studying the hydrolysis thereof [8]. Another group consists of systems based on $CaCl_2$ ($pK_{(4)} \sim 5$, $pI_L \sim 4$) and LiCl ($pK_{(4)} \sim 7$, $pI_L \sim 3.5$) that are hygroscopic salts with rather acidic cations. The dehydration of those salts in vacuum causes formation of CaO and LiOH in small amounts; as a result, the melts thereof are alkalified and give rise to corrosion of platinum or quartz containers. Nevertheless, when a solid chloride is treated with hydrogen chloride gas during heating, its hydrolysis is suppressed completely. The systems based on halides of magnesium and rare-earth elements having $pK_{(4)} < 2$ ($pI_L \geq 6$) could be considered as the third group. Those systems are highly hygroscopic and tend to hydrolysis. The raw material treatment with HCl gas is inefficient due to low $pK_{(4)}$ values. To date, no general rule is developed making it possible to judge the acidity of solid substances. Basing on general consideration, the acidity increases as the cation radius diminishes within one subgroup and is intensified as the element number increases within one period.

Another aspect of importance that defines the extent of hydrolysis is the thermal stability of the corresponding hydrogen halide HX. The stability of hydrogen halides, i.e., their ability of dissociation according to the scheme

$$2HX \uparrow \; \rightleftharpoons H_2 \uparrow + X_2 \uparrow \qquad (8)$$
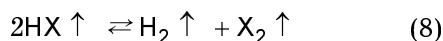
decreases as the anion radius increases (i.e., from chlorine to iodine). Thermodynamic calculation results in values of the corresponding dissociation constants, e.g., $1.74 \cdot 10^{-15}$ for HCl, $1.78 \cdot 10^{-9}$ for HBr and $1.74 \cdot 10^{-2}$ for HI, all at 700 K. In the latter case, the dissociation of hydrogen halide contributes rather considerably to hydrolysis process, since the dissociation extent of HI at the specified temperature attains 18 %, thus favoring a more considerable shift of the process (4) to right as compared to other hydrogen halides. That is, other conditions being the same, iodides tend to hydrolytic decomposition to the most extent [10].

The studies of halogenating agents with oxygen-containing impurities in solid og melted halides consist an important constituent of the acid and base chemistry in high-temperature systems, since the data on corresponding equilibrium constants make it possible to select one substance or another purposed to remove oxygen-containing impurities from a specified ionic halide or halide melt.

In principle, the halogenating agents can be subdivided into two kinds:

— proper acids forming a coupled base with O^{2-} ions;

— redox agents.

According to the Lux-Flood definition [13]:

$$Acid + O^{2-} \rightarrow Weak\ acid + Weak\ base \quad (9)$$
$$2HX + Na_2O \rightarrow H_2O + NaX$$
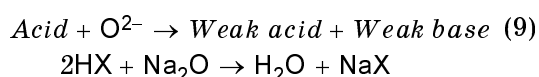
the halogenating agents of the 1st kind exhibit the properties of acids, since their action results in a reduction of oxygen-containing impurity concentration (reduction in the melt basic properties) due to formation of volatile or insoluble (in the melt) oxygen-containing compounds (bases) that are removed from the melt. Considering the second row of (9) and proceeding from the principle of hard and soft acids and bases by Pearson [14], the purification processes using hydrogen halides can be concluded to be thermodynamically favorable as a rule, because the reaction results in products formed by more hard acid and base (H^+ and O^{2-}, respectively) and more soft acid and base (Na^+ and X^-, respectively). Since there is a transition from a hard base to a soft

one in the sequence $Cl^- \rightarrow Br^- \rightarrow I^-$ of halide ions, the process is the least thermodynamically favorable with iodide salts, that being in agreement with the above.

The ammonium halides acting in a double manner can be also included into that group. First, ammonium halides form easily double salts with alkali-earth and rare-earth metals; those salts are the least inclined to hydrolysis and are dehydrated more easily. Second, the purification processes using ammonium halides suppose the sublimation of the latter out of the dehydrated substance. The sublimation of ammonium halides is accompanied by thermal dissociation according to the scheme:

$$NH_4X \xrightarrow{t} NH_3 \uparrow + HX \uparrow, \qquad (10)$$
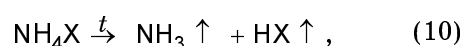
while on cold parts of the container the process runs in the reverse direction. The hydrogen halide thus formed reacts with the oxygen-containing impurities according to reaction reverse to (4), causing an additional purification of the raw mixture. Since water is removed due to the purification, it is expedient to carry out the ammonium halide sublimation in vacuum (usually at 200 to 400°C).

Another way to purification is to use redox processes. The most simplest and the least efficient one is the direct treatment of an ionic halide with a halogen. For the reaction

$$X_2 \uparrow + O^{2-} \; \rightleftharpoons \frac{1}{2}O_2 \uparrow + 2X^- \qquad (11)$$
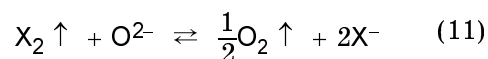
the extent of equilibrium shift to the right depends on the relation between the redox potentials of the halogen and oxygen as well as on acidic properties of the melt (see above).

Proceeding from [15, 16], the oxygen electrode potentials can be estimated in melts containing cations of various acidity. Knowing the potential of the $Ag^+|Ag$ electrode for KCl–NaCl, KCl–LiCl, and KCl–NaCl–SrCl$_2$ melts at 700°C with respect to sodium reference electrode $Na^+|Na$ (~+2.5 V), it is possible to estimate the oxygen electrode potential in solutions with the O^{2-} molality of 10^{-3} mole·kg^{-1} (a melt contaminated with oxygen-containing impurities) to be of +2.85 V for KCl–NaCl and KCl–NaCl–BaCl$_2$, +2.9 V for KCl–NaCl–SrCl$_2$, +3.0 V for KCl–LiCl and KCl–CaCl$_2$, while the chlorine electrode potential is

+3.3 V, the bromine one, −2.5 V, and the iodine one, 2.0 V. It follows therefrom that the melt purification using bromine and iodine is thermodynamically unfavorable, because the potential of those electrodes in all the melts is lower than that of oxygen one. As to chlorine electrode, for chloride melts containing 10^{-3} mole·kg^{-1} O^{2-}, the conditional equilibrium constants are of 10^3 to 10^4. For a KCl–NaCl melt containing 0.05 mole·kg^{-1} of Mg^{2+} cations (a very diluted solution) the K value is 1.6, thus, the purification of such a melt with free chlorine will be no longer efficient. This will be valid also for melts containing rare-earth metal ions in the oxidation degree of +3.

The carbohalogenation process is the sum of the reaction (11) and the following reaction:

$$C \downarrow + \frac{1}{2}O_2 \rightleftarrows CO \uparrow . \qquad (12)$$
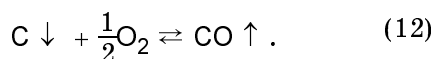
It is just CO rather than CO_2 that is the reaction product, since carbon is introduced usually in a sufficient amount. The equilibrium constant of that reaction within 500−1000°C temperature range varies from $1.5 \cdot 10^{12}$ to $1.6 \cdot 10^9$, i.e., the equilibrium constant of the total process:

$$C \downarrow + X_2 \uparrow + O^{2-} \rightleftarrows CO \uparrow + 2X^- \qquad (13)$$
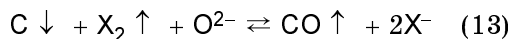
will vary from 10^{16} to 10^{13} for chloride melts, from 10^9 to 10^6 for bromide ones, and from 10^4 to 10^1 for iodide ones with weak acidic properties. As to the strong acidic melts (containing magnesium and REs), the constants will be 3 orders lower. Thus, the removal of oxygen-containing impurities from such melts using carbohalogenation is a difficult problem for bromides and almost insoluble one for iodides.

As it was noted above, the use of most halogenating agents for purification of ionic halides with low acidic properties (alkali and alkali-earth metal salts) provides a positive result in essentially all cases. This is, however, not the case for strong acidic halides (salts of magnesium and REs in the oxidation degree of +3). The fact is that halogen derivatives of hydrocarbons, especially when those contain hydrogen atoms, tend at high temperatures to pyrolysis with formation of the corresponding hydrogen halide. For example, dichloromethane CH_2Cl_2 is decomposed under heating and forms carbon and HCl:

$$CH_2Cl_2 \uparrow \rightleftarrows C \downarrow + 2HCl \uparrow \qquad (14)$$
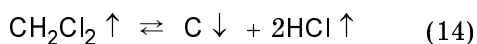
the equilibrium of that reaction being shifted to the right considerably.
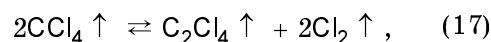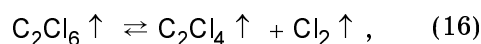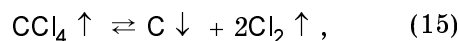
The carbohalogenation process (13) supposes the simultaneous action of the carbon-halogen couple, that is, a redox process. At the same time, in the reaction (14), the products can interact with oxide ions only according to an acid-base reaction. It is obvious that in the case of alkali and alkali-earth halide melts with sufficiently weak acidic properties, the action of CH_2Cl_2 (i.e., C+HCl) and CCl_4 (C+Cl$_2$) will be the same, because the constants of the corresponding equilibria are though very different but exceed 1 by many orders. As to strong acidic melts, the action of halogen substituted hydrocarbons containing hydrogen atoms will be reduced to a reaction reverse to (4) and thermodynamically unfavorable.

The practical realization of carbohalogenation process supposes the halogenating agent introduction into the melt in gaseous state. This, in turn, requires a selected volatile halogen source and the presence of carbon in the melt or in the volatile reagent at the absence of hydrogen; the latter is of a particular importance for the strong acidic melts. For chloride materials, the most suitable halogenating agent is CCl_4, for bromide ones, bromine vapor + carbon black in the melt (CBr_4 has a low vapor pressure and boils at 190°C with decomposition). No suitable combination of reagents has been found for iodide melts.

The carbohalogenation of chloride melts using CCl_4 is carried out as follows. As the raw material is heated under CCl_4 vapor flow in a quartz container up to 500°C, the solid or melted material becomes darkened. The further heating up to 700−800°C results in a gradual clarification of the melt (carbon removal), at the end, it becomes transparent and does not wet the container wall; this fact is a visual sign of the complete removal of oxygen-containing impurities.

Let the processes be considered taking place at the mentioned temperatures:
— pyrolysis of CCl_4

$$CCl_4 \uparrow \rightleftarrows C \downarrow + 2Cl_2 \uparrow , \qquad (15)$$

$$C_2Cl_6 \uparrow \rightleftarrows C_2Cl_4 \uparrow + Cl_2 \uparrow , \qquad (16)$$

$$2CCl_4 \uparrow \rightleftarrows C_2Cl_4 \uparrow + 2Cl_2 \uparrow , \qquad (17)$$

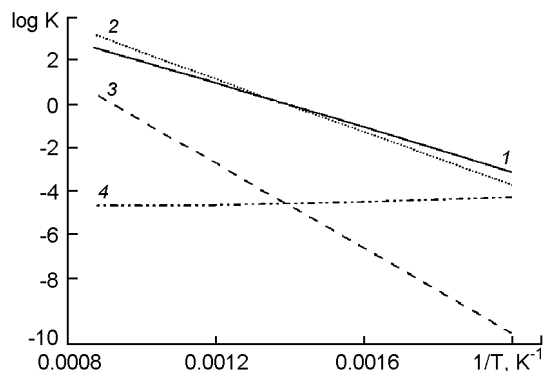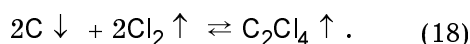— removal of the pyrolysis products from the melt and the gas medium above the melt:

Fig. 2. Temperature dependences of equilibrium constants for reactions (15) (*1*), (16) (*2*), (17) (*3*), (18) (*4*) from inverse temperature.

$$2C \downarrow + 2Cl_2 \uparrow \rightleftarrows C_2Cl_4 \uparrow . \qquad (18)$$

The dependences of the equilibrium constants for the corresponding processes on inverse temperature are shown in Fig. 2.

It is seen from Fig. 2 that at temperatures lower than 700 K ($1/T = 0.0014$), the process (15) predominates over (16), and this fact results in formation of carbon in the mixture or melt and of chlorine. Above 700 K, the processes resulting in formation of gaseous chlorine-containing derivatives (C_nCl_m), mainly C_2Cl_4 (17), and chlorine. A carbon black + chlorine mixture is formed that is just the chlorinating agent. Another process is the carbon removal from the melt due to C_2Cl_4 formation; however, the equilibrium constant of that process is less than 1, so it may run only under removal of the reaction products from the gas atmosphere (in argon flow). This process is rather slow, the melt clarification requires in practice 5 or 6 h. The direct reaction of CCl_4 with carbon is characterized by constants of the order of 10^{-2} to 10^{-3} and runs slowly, too.

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Взаємодія гігроскопічних галогенідів з реакційноздатним газовим середовищем при високих температурах

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Проведено аналіз причин, що ведуть до забруднення іонних галогенідів (лужних, лужноземельних та рідкісноземельних елементів) кисеньвмісними домішками, і чинників, які впливають на процеси гідролізу цих солей. Розглянуто процеси взаємодії розплавів гігроскопічних іонних галогенідів з галогенувальними агентами і встановлено основні закономірності їх перебігу.