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The Oxidation of Zinc and Barium Chlorides with Oxygen to Obtain Chlorine and Finely Dispersed Zinc Oxide

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Abstract—The regular features of the reaction of calcium, barium, and zinc chlorides with oxygen to form molecular chlorine and corresponding metal oxides are studied. The rate constants of the reaction were determined. The effective activation energies of oxidation of chloride ions were calculated with due to regard for the diffusion at the gas-chloride melt interface, which is especially pronounced at a temperature above 550°C. Zinc oxide being formed was separated from the reaction mixture, and the dispersion of its particles was determined.

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Little studies are available on the oxidation of halide ions with oxygen. The reaction of sodium and potassium chlorides with their metaphosphates in an air-argon flow at 800°C has been studied in [1]. It was shown that no chlorine is formed in the absence of oxygen in the system. Kochergin, V.P. et al. [2] also showed that in the reaction of sodium chloride with sodium metaphosphate oxygen serves as oxidant. The reaction of Na(K)Cl with V_2O_5 at 400–600°C in the presence of air yields chlorine and sodium or potassium metavanadates [3–5]. In this case, as oxidant for chloride ions serves oxygen. At the same time, chlorine separation from a molten system in the absence of oxygen also occurs via the reaction of sodium chloride with V_2O_5 with successive formation of vanadium bronzes and sodium metavanadate [6]. In addition to alkali metal metavanadates and V_2O_5, transition metal oxides serve as catalysts in the reaction of oxidation of chloride ions with oxygen in molten sodium, calcium, and zinc halides [7], with their activity correlating with the polarization force of the oxide cation [8].

Certain metal chlorides react with oxygen in the absence of catalysts. For example, the method of chlorine formation via the oxidation of calcium chloride with oxygen at 800°C has been suggested in [9], whereas calcium oxide forming therewith was not separated.

It was established [8] that above 400°C zinc chloride reacts with air oxygen to yield chlorine and the effect of transition metal oxides on the reaction was determined. In addition to the control of chlorine amount separated from molten $ZnCl_2$, the forming zinc oxide was separated and its purity and dispersion was determined. Zinc oxide is a multifunctional semiconducting material, attracting attention of researches as promising catalyst [10, 11], luminophore, and a constituent of light-emitting diodes [12]. The preparation of zinc oxide films by the oxidation of zinc chloride with oxygen at 400°C under decreased pressure has been described in [13]. Therefore, the study of the conditions of the zinc oxide synthesis and the development of methods of its preparation are urgent.

The study is concerned with the regular features of the $ZnCl_2$ oxidation with oxygen, including air oxygen. The kinetic regularities of the formation of chlorine and zinc oxide in oxidation of chloride ions as a function of the type of gas (air or oxygen) upon bubbling through the melt, temperature, and presence of V_2O_5 were determined.

EXPERIMENTAL

We used $ZnCl_2$ and $BaCl_2$ (both pure grade). An amount of the separating chlorine was determined iodometrically [6]. The oxidation was performed within 450–650°C, the air or oxygen was bubbled through the melt or passed over its surface at a rate of 5 l h^{-1}. The error in determining the amount of the forming chloride ions was about 10%.

The zinc oxide separation was studied by dissolving a non-reacted zinc chloride in distilled water. The suspension being formed was centrifuged to separate zinc oxide, which was exhaustively washed to remove all chloride. The absence of chloride ions in the zinc oxide precipitate was controlled by the reaction with a solution of silver chloride. The ZnO powder dried at different temperatures was examined on an Olympus BX51 optical microscope (magnification 100), Solver Pro atomic-force microscope, and on a Hitachi-3400 electron microscope equipped with an energy-dispersive analyzer.

It was found that $ZnCl_2$ oxidation is described by the zero-order equation:

$$ZnCl_2 + 1/2O_2 \leftrightarrows ZnO + Cl_2. \quad (1)$$

Figure 1 demonstrates the dynamics of chlorine separation from a zinc chloride melt upon bubbling air or oxygen through the melt in the temperature range 450–650°C.

The reaction rate in oxidation of zinc chloride with oxygen is higher than in oxidation with air. The oxidation of chloride ions is the zero-order reaction (Table 1), which shows that it is limited by the diffusion of oxygen at the gas–melt interface. Under the similar conditions, the Cl^- oxidation in a $ZnCl_2$ melt proceeds more intensely in oxygen than in air (Table 1). The logarithm of the rate constant of the Cl^- oxidation vs. the inverse temperature is plotted in Fig. 2. The graph has two straight-line portions within 450–550 and 550–650°C in the case of oxygen oxidation and within 500–600 and 600–650°C in the case of air bubbling. The calculated apparent activation energies of the reaction are 116 and 33 kJ mol^{-1} for oxygen, respectively, and 152 and 59 kJ mol^{-1} for air, respectively. The break on the log k–$1/T$ plot and the low E_a^{eff} values of the reaction at high temperatures also confirm the role of oxygen diffusion at the gas–melt interface. In the case of oxidation with oxygen and air, the shift of the temperatures, at which the process passes from the kinetic to diffusion region, is accounted for by the fact that the oxidation rate with oxygen at 823 K and that with air at 873 K are equal and close to the diffusion rate of oxygen and air into the melt at the above temperatures.

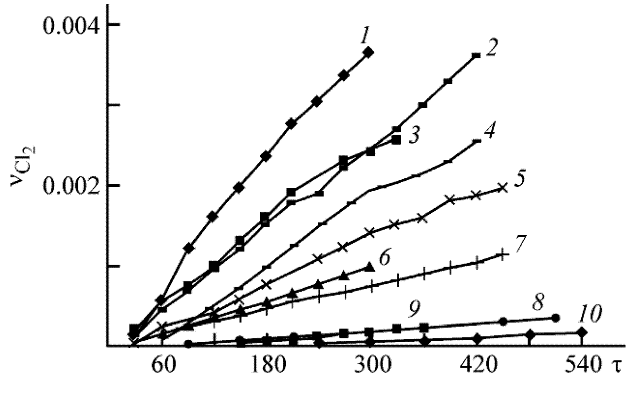

Fig. 1. Dynamics of chlorine separation ν_{Cl2} (mole) from molten $ZnCl_2$ at the rate of the oxygen or air bubbling 5 l h^{-1}. (τ) Time (min); the same for Fig. 3. (*T*) (°C), medium: (*1*) 650, O_2; (*2*) 600, O_2; (*3*) 650, air; (*4*) 550, O_2; (*5*) 600, air; (*6*) 575, air; (*7*) 500, O_2; (*8*) 450, O_2; (*9*) 550, air; (*10*) 500, air.

Table 1. The rate constants of Cl^- oxidation and amount of chlorine separated from $ZnCl_2$ during 300 min of bubbling air or oxygen through the melt

T, °C	ν_{Cl2}, mole		$k_0 \times 10^8$, mol s^{-1}	
	Air	O_2	Air	O_2
450	–	0.00019	–	1.26 ± 0.04
500	0.00002	0.00071	0.64 ± 0.02	4.25 ± 0.58
550	0.00016	0.00191	1.25 ± 0.07	13.07 ± 1.00
575	0.00031	–	5.79 ± 0.58	–
600	0.00138	0.00244	9.11 ± 0.66	17.02 ± 0.04
650	0.00242	0.00363	14.37 ± 0.25	22.03 ± 1.63

We studied the formation of molecular chlorine in calcium and barium melts. Chloride ions were oxidized in air or oxygen at 800°C. From barium chloride, no chlorine was separated in air up to the melting point of $BaCl_2$ (960°C), whereas in oxygen, a weak Cl_2 separation was observed only after 240 min elapsed after the beginning

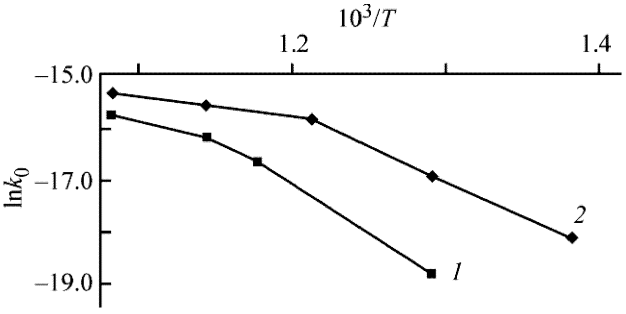

Fig. 2. The logarithm of the rate constant ln k_0 of the chloride ion oxidation in (*1*) air and (*2*) oxygen vs. the inverse temperature $1/T$ (K^{-1}).

of the process. Note, the onset of the molecular chlorine separation from calcium chloride is at 380–400°C. In this case, the reaction proceeds by the zero order, like the reaction with oxygen. The rate constant of the chloride ion oxidation in a calcium chloride melt at 800°C upon bubbling air through the melt is $(9.57 \pm 0.62) \times 10^{-8}$ mol s^{-1}, which is comparable with the rate constant of the reaction in a zinc chloride melt at 600°C (Table. 1). Thus, calcium chloride is less active oxidant for Cl^- than zinc chloride.

The ability of ions to exert a mutual polarization effect plays the important role in their chemical behavior [14]. In this connection, it was interesting to compare the reactivity of the chlorides under study in oxidation of chloride ions with the polarization force of their cations. The polarization force of the chlorine anion may be neglected owing to its small charge and relatively large ionic radius [14]. According to the estimation criteria presented in [14], the polarization force of the cations should decrease in the order $Zn^{2+} > Ca^{2+} > Ba^{2+}$. The performed calculations confirmed the above order. The polarization force of the cations was determined by the formula:

$$ze/r_{M^{z+}}, \quad (2)$$

where z is the charge of the cation, $e = 4.803 \times 10^{-10}$ esu is the elementary charge, and $r_{M^{z+}}$ is the cation radius.

Table 2 collects the radii of the Zn^{2+}, Ca^{2+}, and Ba^{2+} cations, their polarization forces, and the chlorine amount separated from corresponding chlorides.

As seen from Table 2, the chlorine amount separated from metal chlorides depends on the polarization force of the chloride cation: the higher the $ze/r_{M^{z+}}$ ratio, the stronger the deformation effect exerted by the cation on the chloride ion [14] and the more intense the Cl^- oxidation.

We studied the reaction of calcium, barium, and zinc chlorides with vanadium pentoxide. It was shown that the addition of 10 wt % of V_2O_5 to the chloride increases the chlorine amount separated from the mixture in comparison with that separated from individual chloride. The effect of vanadium oxide on the barium chloride oxidation is the most marked. In air, no chlorine is separated from $BaCl_2$ at 800–960°C, whereas in the presence of 10 wt % of vanadium oxide it is separated. The addition of vanadium oxide to calcium and zinc chlorides also increases the amount of separated chlorine in comparison with individual chlorides $CaCl_2$ and $ZnCl_2$. In this case, the dependence of the catalytic effect of V_2O_5 on the chloride ion oxidation in the melts of the above chlorides also has the inverse order (Fig. 3). The cations are arranged in the following order with respect to the amount of the separated chlorine $Zn^{2+} > Ca^{2+} > Ba^{2+}$. The results obtained agree with the order Ca–Sr–Ba, in which carbonates in a mixture with V_2O_5 are arranged with respect to increasing reactivity [15].

Table 2. The polarization force of the cations and the amount of chlorine separated from MCl_2 during 300 min of bubbling air or oxygen through the melt

Cation	$r_{M^{z+}}$, nm	$ze/r_{M^{z+}}$, esu cm^{-1}	T, °C	ν_{Cl_2}, mole
Ba^{2+}	0.138	0.070	960	0
Ca^{2+}	0.104	0.092	800	0.00154
Zn^{2+}	0.083	0.116	650	0.00242

Figure 4 demonstrates the dependence of the chlorine amount separated from the MCl_2–V_2O_5 systems on the polarization force of the chloride cation. The above dependence is described by the following equation:

$$N_{Cl_2} = -14.662x + 1.8493,$$

where x is the polarization force of the cation; the correlation coefficient is 0.9780.

Among the ions studied, the least polarization force is exhibited by the barium cation. Therefore, the effect of V^{5+} on its deformability will be larger than for other cations. The sodium cation falls out of this order. Its po-

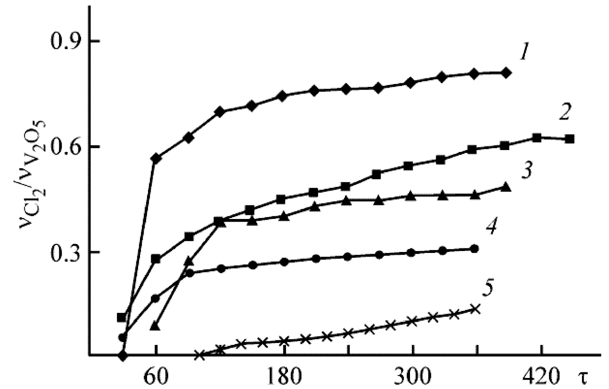

Fig. 3. The relative amount of chlorine ν_{Cl2}/ν_{V2O5} (mole/mole) released from the MCl_2–10 wt % V_2O_5 system upon passing the air over the melt of 30 g weight. (*1*) $BaCl_2$, (*2, 3*) $CaCl_2$, (*4*) NaCl, and (*5*) $ZnCl_2$. v (l h^{-1}): (*1, 2*) 5 and (*3–5*) 2.5. T (°C): (*1–4*) 800 and (*5*) 600. Reference: (*3*) [8] and (*4*) [7].

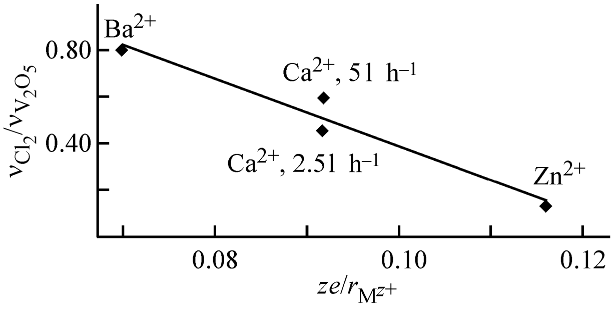

Fig. 4. The relative amount of chlorine $\nu_{Cl_2}/\nu_{V_2O_5}$ (mole/mole) released from the MCl_2–10 wt % V_2O_5 systems vs. the polarization force of the chloride cation $ze/r_{M^{z+}}$.

larization force is lower than of barium cation, whereas the effect of vanadium pentoxide on its oxidation ability with respect to chloride ions is lower too (Fig. 3, curve *4*). This is accounted for by the low deformation ability of its electronic shells.

Metal oxides possess higher melting temperatures than corresponding chlorides. Also, they have low solubility in chlorides. Therefore, in halide melts they will be in the form of a precipitate, because their density is higher than that of oxides. For example, the density of ZnO is 5.7 and that of $ZnCl_2$, 2.91 g cm^{-3} [16]. In this case, the oxide particles formed will be stabilized (solvated) with molten metal chlorides, which gives hope to obtain highly dispersed oxide powders.

The size of the obtained zinc oxide particles lies within 200–700 nm. Sometimes, particles with less than 50–100 nm were formed. A broad dispersion interval of the zinc oxide particles is accounted for by the conditions of the oxide synthesis. The high temperature (600°C) and the long time (~20 h) of the zinc chloride oxidation facilitate recrystallization processes. As known, a particle growth mostly proceeds by the dissolution-crystallization mechanism (known as Ostwald ripening). Therefore, the size of forming oxide particles depends on the solubility of the oxides formed in a metal chloride melt and on the process temperature and time. The elemental analysis of the ZnO sample confirmed presence of the following elements (at. %): Zn 39.16, O 60.76, and Cl 0.09. Some samples contained silicon, which probably penetrated from the reactor and bubbler pipe made of quartz. A high content of oxygen is ascribed to zinc hydroxide, which is present in the sample along with zinc oxide. The specific surface area of the obtained powder is 0.77 m^2 g^{-1}.

CONCLUSIONS

(1) With increasing polarization force of the cations, the oxidation ability of chloride ions in melts of zinc, calcium, and barium chlorides increases, whereas the catalytic effect of vanadium pentoxide on this process decreases.

(2) The oxidation of chloride ion in a molten zinc chloride is the zero-order reaction, limited by the diffusion of oxygen above 550°C.

(3) The size of the zinc oxide particles obtained by $ZnCl_2$ oxidation changes in the range 50–700 nm, which is due to high temperature of the experiment and its long time.

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