5. Ruthven D. M., Kenney C. N.: J. Inorg. Nucl. Chem. *20*, 931 (1968).
6. Sláma I.: This Journal *28*, 518 (1963).
7. Sláma I., Regner A.: This Journal *31*, 915 (1966).
8. Sláma I., Regner A.: This Journal *31*, 970 (1966).
9. Kenney C. N.: *Fourth Intern. Congress on Catalysis, Moscow 1968.* Preprint of paper 86.

CATALYTIC OXIDATION OF HYDROGEN CHLORIDE WITH OXYGEN IN MELTS OF COPPER CHLORIDES

I.Sláma and J.Pacák

Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, Prague 6

In our previous paper[1] we studied the kinetics of oxidation of cuprous chloride with a mixture of oxygen and hydrogen chloride in melts. We have ascertained that the oxidation rate of cuprous chloride does not depend on its concentration in the melt. This finding was explained by assuming a reaction of oxygen with hydrogen chloride, taking place at the surface of the melt which causes that the composition of the contact surface layers is different from that of the bulk of the melt. The composition of contact layers changes only unsignificantly and consequently also the rate of reactions which is determined by absorption, is independent of the average concentration of cupric chloride in the melt. Under this assumption the oxidation of hydrogen chloride with oxygen should proceed in the given region at a practically constant rate, too. According to the presumed mechanism of catalytic effects of melts the rate determining step is the absorption of oxygen which is followed by the fast, practically irreversible reaction of the formed oxichloride with hydrogen chloride[2-4]. The formed cupric chloride is in equilibrium with chlorine in the gaseous phase. Since the governing factor in this equilibrium is the concentration of cupric chloride at the interphase boundary, the oxidation rate of hydrogen chloride at the beginning of the reaction should be much greater than would correspond to the average concentration of cupric chloride in the melt. This could serve as a proof of the assumption that the concentration of cupric chloride at the surface of contact layer is greater.

The second aim of the present study was to verify the kinetic equation of catalytic oxidation of hydrogen chloride by oxygen at the surface of molten copper chlorides, as it was derived by Kenney[2]. This equation is based on the assumption that the concentration of chlorine in the gaseous phase, which is a function of hydrogen chloride conversion, *i.e.* of the reaction rate and of the partial pressure of hydrogen chloride, determines unambiguously the ratio of cupric chloride to cuprous chloride in the melt. In this way it also determines the reaction rate, as the absorption rate of oxygen depends on the square of cuprous chloride concentration. Experimental verification of this presumption, however, is not quite convincing, as in the steady state catalysis the ratio of cuprous to cupric chlorides is always greater than unity and changes

within relatively narrow limits. In the oxidation of cuprous chloride with a mixture of oxygen and hydrogen chloride the concentration ratio of cuprous to cupric chlorides changes during the experiments, ranging from 0 to c. 4. Therefore in this case the most decisive would be to verify the kinetic equation.

EXPERIMENTAL

Apparatus, chemicals used as well as analytical procedures were the same as described in our previous paper[1]. Unless otherwise stated, an equimolar mixture of oxygen and hydrogen chloride was used, at flow-rate 200 ml/min and at 500°C.

RESULTS AND DISCUSSION

A typical course of the oxidation rate of hydrogen chloride in the reaction of cuprous chloride with a mixture of oxygen and hydrogen chloride is shown in Fig. 1. The oxidation rate of hydrogen chloride, R, reaches within a few minutes a practically constant value which then increases only slightly up to 150 min. The experimentally determined reaction rate for this region (curve 1) differs from that which could be expected from the dependence of kinetics of thermal decomposition of cupric chloride in the bulk of the melt[1]. The theoretically derived course of oxidation rate of hydrogen chloride was plotted in the same graph (curve 2). Comparison of the experimental course of oxidation with that calculated according to our previous work reveals that the oxidation rate of hydrogen chloride is, in the first half of the experiment, much greater than would correspond to the theoretically assumed course. However, this finding agrees with the
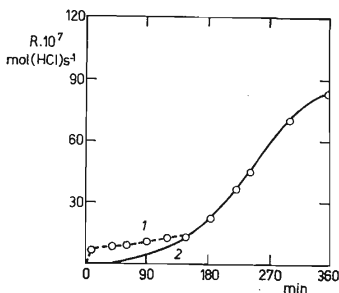

Fig. 1

Rate of Oxidation of Hydrogen Chloride (R) in Melt Oxidation with a Mixture of Oxygen and Hydrogen Chloride

50 mol % KCl, 500°C, $P_{O_2} = P_{HCl} = 0.5$ atm. 1 Experimental values, 2 values calculated from the composition of the melt.
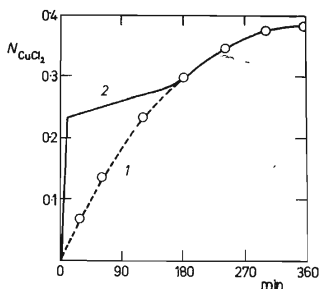
Fig. 2

Course of Cuprous Chloride Oxidation in the Melt

50 mol % KCl, 500°C, $P_{O_2} = P_{HCl} = 0.5$ atm. 1 Experimental values, 2 calculated from the oxidation rate of hydrogen chloride.

mechanism of cuprous chloride oxidation in melts with a mixture of oxygen and hydrogen chloride, as proposed in our earlier work. In order to explain the zero-th order of this reaction with respect to the concentration of cuprous chloride we assumed that oxygen reacts directly with the melt surface to form cupric oxichloride which is transformed into cupric chloride in a fast reaction with hydrogen chloride. This causes an increase in cupric chloride concentration at the interphase boundary melt–gas. Since the concentration of cuprous chloride on the contact surface which is decisive for the kinetics of oxygen absorption, does not change too much in the first half of the experiment, it is possible to explain the independence of the oxidation rate of cuprous chloride in the melt of its average concentration in the bulk of the melt.

If the above explanation is valid, then also the concentration of cupric chloride at the contact surface undergoes no significant change in the first half of the kinetic measurement. However, its value is much greater than is the average concentration of cupric chloride in the bulk of the melt. The rate of cupric chloride decomposition or the oxidation of chloride ions by ions of bivalent copper depends on the composition of the contact layer surface and therefore the oxidation rate of hydrogen chloride in the first stage of kinetic experiment can be independent of the average concentration of cupric chloride in the bulk of the melt. This fact may serve as proof of the conception assuming a concentration gradient in the surface contact layers of the melt on which our mechanism of cuprous chloride oxidation by a mixture of oxygen and hydrogen chloride was based.

We have calculated theoretical values of cupric chloride concentration at the surface of contact layer, being in equilibrium with the gaseous phase. The data are plotted in Fig. 2 (curve 2). It is evident from the comparison of the course of curve 2 with the experimentally found values of the average concentration of cupric chloride in the bulk of the melt that already within a few minutes the composition of the contact layer becomes different from the average composition of the melt. This difference decreases in the course of the experiment, since the composition of the contact layer does not change significantly, whereas the average concentration of cupric chloride in the melt increases. If the average concentration of cuprous chloride reaches the value, corresponding to the composition of the contact mass, an increase in cupric chloride concentration takes place which in the further course of the experiment, is the same both in the contact layer and in the bulk of the melt.

From this comparison it follows that a verification of the kinetic equation of catalytic oxidation of hydrogen chloride by oxygen on the surface of melts based on copper chlorides is impossible in the region of lower cupric chloride concentrations. The relation, derived by Kenney for this process in a steady state, has the form:

$$R_s = 4 \cdot k \cdot j^2 \cdot K^2 \cdot a^2 \cdot P_{O_2}/(j \cdot K + \sqrt{P_{Cl_2}})^2 , \qquad (1)$$

where R is the specific reaction rate (mol (HCl)/s . cm²), k is the rate constant, corresponding to the absorption rate constant of oxygen on melts of the copper chloride type, jK is the product of activity coefficients and of the equilibrium constant of the reaction $CuCl_2 = CuCl + \frac{1}{2} Cl_2$ and a is the mole fraction of copper chlorides in the melt. In deriving this equation Kenney assumed the absorption of oxygen to be the rate determining step of the whole catalyzed process. Thus it can be stated concluded that relation (1) holds only for a steady state. From the practical point of view, this region is of course the most important one.

By means of kinetic equation (1) it is now possible to compare our maximum values of the reaction rate R_r with the data of Kenney. In his paper[2] some data, necessary for the calculation, are not presented and therefore we employed the values of specific absorption rate of oxygen, k_3, from the earlier paper by Ruthven and Kenney[3]. The product of activity coefficients and of equilibrium constant was evaluated from thermodynamic data of systems, similar to which are

given by Ruthven and Kenney in another publication[4]. The calculated values of specific reaction rate (R_s) together with our data (R_r) are summarized in Table I. These values cannot be compared directly, as in our experimental arrangement it is difficult to determine exactly the surface area of the contact surface. However, we can assume that the contact surface does not change in individual experiments, its value being of the order of tens of square centimeters. Consequently, the ratio R_s/R_r should express the contact surface area; it is presented in the 1st column of Table I. From the values it is evident that a good agreement was obtained of our data with those calculated using relation (I). Particularly in the case of melts containing neodymium chloride the accordance is very good: the calculated value of R_r/R_s corresponds to the estimated contact surface area of our experimental arrangement.

The oxidation rate of hydrogen chloride in melts containing admixture of neodymium chloride is rather high and in this region the kinetic equation derived by Kenney may be unvalid. Using the thermodynamic data for the equilibrium of reaction[5]

$$4 \, HCl \, + \, O_2 \;\; = \;\; 2 \, Cl_2 \, + \, H_2O \, , \tag{A}$$
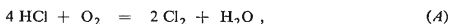
we calculated the value of equilibrium conversion of hydrogen chloride and from this also the value of the maximum possible reaction rate R_r which at the given composition of the gaseous phase and at 500°C was equal to 500. 10^{-7} mol (HCl)/s. Comparing the values of R_r with the above value we found that in melts containing neodymium chloride the conversion of hydrogen chloride amounts to 66 to 86% of the maximum possible values. Analysis of kinetic equation (I) allows to conclude that this relation cannot hold in the region of high values of hydrogen chloride conversion, as it does not comprise the rate of the reverse reaction and therefore it is not thermodynamically consistent. However, the comparison indicates the possibility to employ kinetic equation (I) even in the region where the conversion of hydrogen chloride exceeds 70% of the maximum possible value.

At lower partial pressures of hydrogen chloride the values of R_r/R_s were considerably lower, owing to the fact that a practically constant conversion was reached and the oxidation rate of hydrogen chloride did not correspond to relation (I), being limited by the thermodynamic equilibrium of reaction (A).

TABLE I

Rate of Oxidation of Hydrogen Chloride with Oxygen in the Steady State (R_r) and Specific Reaction Rate (R_s)

500°C, $P_{O_2} = P_{HCl} = 0.5$ atm.

KCl mol %	NdCl$_3$ mol %	$R_r \cdot 10^7$ mol s^{-1}	$R_s \cdot 10^7$ mol s^{-1} cm^{-2}	$R_r/R_s = A$ cm^2
30	0	133	4·3	31
40	0	125	2·6	48
50	0	83	1·4	59
27·3	9	384	8·1	47
36·4	9	433	8·3	52
45·5	9	366	7·5	49

The effect of addition of rare earths chlorides to the melts used for catalysis is most distinctly manifested with equimolar mixture of potassium and cuprous chlorides. In this case the oxidation rate of hydrogen chloride is about 5 times greater. Contrary to this the absorption rate of oxygen increases by the addition of rare earths chlorides 20 times. This apparent disproportion can be explained by the fact that increasing partial pressure of chlorine causes a decrease in the value of rate of hydrogen chloride oxidation according to relation (*1*). At high conversions of hydrogen chloride the oxidation rate is practically indirectly proportional to the partial pressure of chlorine, as $\sqrt{P_{Cl_2}} \gg jK$. Consequently the effect of rare earths on the oxidation rate of hydrogen chloride is less than in the case of absorption rate of oxygen.

An interesting point is the quantitative interpretation of the effect of concentration of rare earths chlorides on the oxidation rate of hydrogen chloride. We have tried to express the relation between he rate constant and the concentration of lanthanum chloride, as taken from the data of Kenney[3], in terms of an empirical equation. We have found that the rate constant can be correlated in the form

$$k = B' + D' N^2_{LaCl_3}, \tag{2}$$

where k denotes the rate constant from Eq. (*1*), B' and D' are empirical constants and N_{LaCl_3} is the mole fraction of lanthanum chloride in the melt. The values of B' and D' at 500°C are $10 \cdot 10^{-7}$ and $4 \cdot 95 \cdot 10^{-3}$, respectively.

Rare earths chlorides can thus be assumed to form an associate with cuprous chloride, the reactivity of which in the course of oxygen absorption is greater by the order of magnitude than the reactivity of cuprous chloride and the concentration of which is proportional to the products of mole fractions of cuprous chloride and rare earths chloride. The great reactivity of this hypothetical associate is probably caused by the different configuration (sterical arrangement) of copper atoms, favourable for binding oxygen molecule.

REFERENCES

1. Sláma I., Pacák P.: This Journal, in press.
2. Kenney C. N.: *Fourth Intern. Congress on Catalysis, Moscow 1968.* Preprint of paper 86.
3. Ruthven D. M., Kenney C. N.: Chem. Eng. Sci. *22*, 1561 (1967).
4. Ruthven D. M., Kenney C. N.: J. Inorg. Nucl. Chem. *30*, 931 (1968).
5. Arnold Ch. W., Kobe K. A.: Chem. Eng. Prog. *48*, 293 (1952).

Translated by V. Čermáková.