

OXIDATION OF HYDROGEN CHLORIDE WITH OXYGEN,
CATALYZED BY COPPER CHLORIDES
DEPOSITED ON A CARRIER

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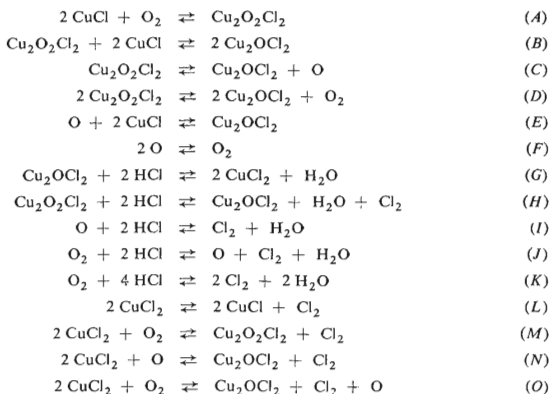
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Catalytic oxidation of hydrogen chloride has recently been given a great deal of attention¹⁻⁶. This interest originated from both practical and theoretical aspects. Catalysts based on copper chlorides represent a typical case of catalytic effect of molten salts on reactions proceeding in the vapour phase. For this reason most of the papers were devoted to the vapour phase-molten salt interaction.

From the practical point of view, however, the fixing of the melt in a suitable carrier is of greater importance. This system is more difficult both with respect to experimental investigation and to the interpretation of results. Its studium involves not only the current problems of heterogeneous catalysis (effect of transport processes on reaction kinetics, utilization of the internal surface of catalyst, *etc.*) but it becomes even more intricately by the hardly reproducible formation of liquid film in the carrier pores. Therefore it seemed of interest, whether it would be possible to apply the results of studies of molten salts reactions to the process of heterogeneous catalysis with active substances, deposited in the carrier pores. The aim of the present work was to verify this possibility.

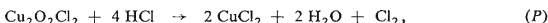
THEORETICAL

Catalytic effect of copper chlorides in hydrogen chloride oxidation with oxygen can be interpreted in terms of the following sequence of theoretically possible simultaneous reactions:

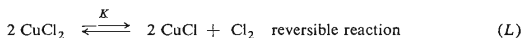
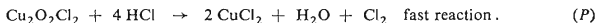
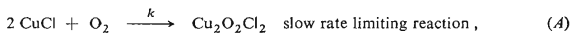


Reactions (A) to (F) are identical with those which can possibly proceed in the absorption of oxygen with cuprous chloride melts. Eqs (G)–(K) describe the possible reactions of intermediates and of oxygen with hydrogen chloride, or, *vice versa*, reactions of water vapour with intermediates and with products of the catalytic process. (L) to (O) are possible reactions of cupric chloride or, reversely, the reactions of chlorine with cuprous chloride or with intermediates. This system is rather complicated for quantitative treatment and therefore we thought of possible simplifications. Some reactions do not proceed in an ascertainable extent and some of them are very fast so that they cannot affect the kinetics of the resulting process. This was taken into account when analyzing the course of individual reactions.

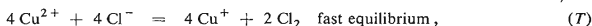
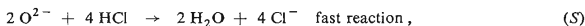
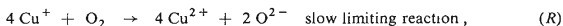
Reaction (A) is the kinetically limiting process in the absorption of oxygen in cuprous chloride melts. Consequently, the kinetics of this reaction has to be considered in making a total estimate. Reaction rate of reactions (B) to (J) is by some orders higher than that of reaction (A). Reactions (J) and (K) are homogeneous reactions in the vapour phase which do not practically proceed at the given temperatures. Reaction (L) is a fast reversible reaction and therefore in the calculation we can suppose that the reaction components are in equilibrium. Reactions of oxygen with cupric chloride do not probably proceed in any detectable extent, as no chlorine was found in the vapour phase in the case of oxygen absorption in melts. Taking further into account that the fast reactions of peroxichloride and oxichloride decomposition can be combined into one single step



for the reaction order of these reactions is without effect on the resulting kinetic equation, we can finally obtain the following simplified scheme



According to the mechanism reported earlier⁴



oxygen absorption with cuprous chloride would necessarily be a fourth-order reaction with respect to cuprous chloride concentration. Such an interaction of five particles is improbable. Second-order reaction was found experimentally which is in agreement with the suggested scheme (A), (P) and (L).

Reaction rate of oxygen absorption by cuprous chloride in a unit contact area can be calculated according to the relation

$$\frac{dn_{\text{O}_2}/dt}{S} = k_A[\text{CuCl}]^2 \cdot P_{\text{O}_2}, \quad (I)$$

where S is the contact surface area in cm^2 and n_{O_2} stands for the number of mol of oxygen.

Oxidation rate of hydrogen chloride is, according to stoichiometry, defined by the quotient

$$R = \frac{dn_{\text{HCl}}/dt}{S} = 4k_A[\text{CuCl}_2]^2 P_{\text{O}_2} \quad (2)$$

If we substitute for cuprous chloride concentration the equilibrium concentration from reaction (L)

$$K_L = [\text{CuCl}]^2 \cdot P_{\text{Cl}_2} / [\text{CuCl}_2]^2 \quad (3)$$

we obtain the kinetic equation of reaction rate in the form

$$R = 4k_A K_L [\text{CuCl}_2]^2 \cdot P_{\text{O}_2} / P_{\text{Cl}_2} = k' P_{\text{O}_2} / P_{\text{Cl}_2} \quad (4)$$

This equation expresses the dependence of reaction rate on partial pressures of oxygen and chlorine for a given composition of the catalytically active substance. The effect of the active substance composition is included in the rate constant k' which is the product of the values of oxygen absorption constant k_A , cupric chloride dissociation equilibrium constant K_L and the square of cupric chloride concentration. At constant composition of the active substance the reaction rate is directly proportional to the partial pressure of oxygen and indirectly proportional to that of chlorine.

The catalytic process can be interpreted in terms of the mentioned reaction rate equation only within a certain range of hydrogen chloride conversion to chlorine, since the effect of the reversed reaction is neglected. Therefore this relation is not thermodynamically consistent. Preliminary experiments showed that the reversed reaction of chlorine with water vapour is practically without effect even in conversions, attaining 50% of the theoretically possible conversion. In this region partial pressure of hydrogen chloride and of water vapour has practically no effect on the reaction rate.

EXPERIMENTAL

Apparatus, Chemicals Used and Analytical Methods

A differential flow reactor was used, consisting of a system of interjoined U-shaped tubes (inner diameter 6 mm). Each of these tubes had a separate gas inlet or outlet, and the catalytic bed was placed in the vertical part of the U-tube. One of the tubes served as the differential reactor proper. The other reactors were used to obtain mixtures of reacting gases with different chlorine content. By inserting one or more tubes before the differential reactor, the composition of the fed-in gas could be stepwise changed in a quite simple way. The U-tubes were thermostated in a stirred bath of molten alkali nitrates, with an accuracy of $\pm 1^\circ\text{C}$.

RESULTS AND DISCUSSION

The found values of reaction rate were recalculated for unit contact surface and are summarized in Table I, together with the values of reaction rates, evaluated according to the above mentioned rate equation. The data used for calculations were the following: the value of k_A is in the measured region independent of temperature and for the used active substance, containing equimolar amounts of copper chlorides and potassium chloride, depends on the content of neodymium chloride.

| | | | | | | | |
|---|----|----|----|-----|-----|-----|------|
| mol % NdCl_3 | 0 | 2 | 4 | 6 | 8 | 10 | 33.3 |
| $k_A \cdot 10^7$ | 24 | 40 | 90 | 170 | 280 | 450 | 700 |
| $\text{mol s}^{-1} \text{cm}^2 \text{atm}^{-1}$ | | | | | | | |

TABLE I
Experimental and Calculated Values of Reaction Rate

| P_{O_2} atm | P_{Cl_2} atm | $N_{CuCl_2}^2$ | $R_{calc} \cdot 10^7$ mol s ⁻¹ cm ⁻² | $R_{exp} \cdot 10^7$ mol s ⁻¹ cm ⁻² |
|--|-------------------|----------------|---|--|
| Catalyst: 33 mol % NdCl ₃ , 400°C | | | | |
| 0.174 | 0.029 | 0.083 | 0.97 | 0.99 |
| 0.168 | 0.044 | 0.087 | 0.65 | 0.70 |
| 0.171 | 0.014 | 0.074 | 1.77 | 1.82 |
| 0.163 | 0.055 | 0.089 | 0.52 | 0.53 |
| 0.159 | 0.066 | 0.091 | 0.43 | 0.40 |
| 0.171 | 0.014 | 0.074 | 1.77 | 1.78 |
| 0.360 | 0.038 | 0.086 | 1.60 | 1.62 |
| 0.355 | 0.054 | 0.089 | 1.15 | 1.28 |
| 0.351 | 0.066 | 0.091 | 0.95 | 0.90 |
| 0.542 | 0.044 | 0.087 | 2.10 | 2.08 |
| 0.541 | 0.050 | 0.089 | 1.89 | 1.92 |
| 0.535 | 0.070 | 0.091 | 1.36 | 1.24 |
| 0.733 | 0.042 | 0.087 | 2.98 | 2.93 |
| 0.732 | 0.047 | 0.088 | 2.69 | 2.83 |
| 0.728 | 0.068 | 0.091 | 1.91 | 1.86 |
| 420°C | | | | |
| 0.172 | 0.034 | 0.078 | 1.43 | 1.41 |
| 0.169 | 0.040 | 0.080 | 1.22 | 1.21 |
| 0.364 | 0.023 | 0.073 | 4.20 | 4.35 |
| 0.362 | 0.031 | 0.076 | 3.22 | 3.44 |
| 0.360 | 0.035 | 0.078 | 2.92 | 2.84 |
| 0.358 | 0.042 | 0.080 | 2.48 | 2.37 |
| 0.552 | 0.025 | 0.074 | 5.93 | 5.88 |
| 0.546 | 0.051 | 0.082 | 3.18 | 3.23 |
| 0.797 | 0.023 | 0.073 | 9.18 | 9.10 |
| 0.796 | 0.029 | 0.076 | 7.57 | 7.45 |
| 0.794 | 0.046 | 0.081 | 5.08 | 4.85 |
| 0.793 | 0.054 | 0.083 | 4.43 | 4.60 |
| Catalyst: 6 mol % NdCl ₃ , 400°C | | | | |
| 0.735 | 0.078 | 0.184 | 0.82 | 0.76 |
| 0.738 | 0.057 | 0.179 | 1.10 | 1.19 |
| 0.743 | 0.025 | 0.162 | 2.29 | 2.20 |
| 0.731 | 0.006 | 0.121 | 7.01 | 6.95 |
| 0.728 | 0.020 | 0.157 | 2.71 | 2.60 |
| 0.731 | 0.006 | 0.122 | 7.06 | 7.11 |
| 0.546 | 0.016 | 0.150 | 2.44 | 2.44 |
| 0.542 | 0.029 | 0.166 | 1.48 | 1.53 |
| 0.362 | 0.013 | 0.146 | 1.93 | 1.78 |

TABLE I
(Continued)

| P_{O_2} atm | P_{Cl_2} atm | $N_{CuCl_2}^2$ | $R_{calc} \cdot 10^7$ $mol\ s^{-1}\ cm^{-2}$ | $R_{exp} \cdot 10^7$ $mol\ s^{-1}\ cm^{-2}$ |
|-------------------------------------|-------------------|----------------|---|--|
| 0.355 | 0.032 | 0.167 | 0.88 | 0.88 |
| 0.175 | 0.018 | 0.154 | 0.71 | 0.68 |
| 0.173 | 0.023 | 0.160 | 0.57 | 0.55 |
| 0.167 | 0.038 | 0.171 | 0.36 | 0.38 |
| 0.177 | 0.003 | 0.103 | 2.89 | 2.64 |
| 420°C | | | | |
| 0.707 | 0.013 | 0.128 | 6.13 | 5.71 |
| 0.706 | 0.020 | 0.141 | 4.38 | 4.30 |
| 0.705 | 0.027 | 0.149 | 3.42 | 3.62 |
| 0.704 | 0.032 | 0.153 | 2.96 | 2.92 |
| 0.528 | 0.010 | 0.121 | 5.62 | 5.40 |
| 0.527 | 0.016 | 0.134 | 3.88 | 3.52 |
| 0.524 | 0.028 | 0.150 | 2.48 | 2.60 |
| 0.356 | 0.009 | 0.117 | 4.07 | 3.82 |
| 0.354 | 0.014 | 0.131 | 2.92 | 2.74 |
| 0.351 | 0.024 | 0.145 | 1.87 | 1.70 |
| 0.176 | 0.007 | 0.107 | 2.36 | 2.46 |
| 0.174 | 0.011 | 0.121 | 1.68 | 1.89 |
| 0.172 | 0.015 | 0.132 | 1.33 | 1.38 |
| 380°C | | | | |
| 0.711 | 0.005 | 0.144 | 4.86 | 4.84 |
| 0.710 | 0.010 | 0.161 | 2.72 | 2.82 |
| 0.708 | 0.021 | 0.177 | 1.42 | 1.49 |
| 0.707 | 0.026 | 0.181 | 1.17 | 1.14 |
| 0.711 | 0.005 | 0.142 | 4.80 | 4.60 |
| 0.531 | 0.004 | 0.138 | 4.35 | 3.94 |
| 0.530 | 0.008 | 0.157 | 2.48 | 2.30 |
| 0.527 | 0.023 | 0.178 | 0.97 | 0.97 |
| 0.349 | 0.007 | 0.154 | 1.83 | 1.76 |
| 0.347 | 0.015 | 0.171 | 0.94 | 0.81 |
| 0.175 | 0.002 | 0.121 | 2.52 | 2.40 |
| 0.174 | 0.005 | 0.144 | 1.19 | 1.29 |
| 0.171 | 0.011 | 0.164 | 0.61 | 0.59 |
| 0.170 | 0.014 | 0.169 | 0.49 | 0.49 |
| Catalyst: 4 mol. % $NdCl_3$, 400°C | | | | |
| 0.183 | 0.002 | 0.092 | 2.12 | 2.00 |

TABLE I
(Continued)

| P_{O_2} atm | P_{Cl_2} atm | $N_{CuCl_2}^2$ | $R_{calc} \cdot 10^7$ $mol\ s^{-1}\ cm^{-2}$ | $E_{exp} \cdot 10^7$ $mol\ s^{-1}\ cm^{-2}$ |
|-------------------------------------|-------------------|----------------|---|--|
| 0.181 | 0.006 | 0.129 | 0.98 | 0.86 |
| 0.366 | 0.012 | 0.150 | 1.15 | 1.07 |
| 0.548 | 0.008 | 0.139 | 2.40 | 2.24 |
| 0.547 | 0.013 | 0.152 | 1.61 | 1.44 |
| 0.546 | 0.018 | 0.161 | 1.23 | 1.34 |
| 0.544 | 0.026 | 0.170 | 0.89 | 0.82 |
| 0.734 | 0.009 | 0.142 | 2.91 | 2.65 |
| 0.733 | 0.015 | 0.155 | 1.91 | 1.91 |
| 0.731 | 0.028 | 0.171 | 1.13 | 1.20 |
| Catalyst: 2 mol. % $NdCl_3$, 400°C | | | | |
| 0.176 | 0.004 | 0.116 | 0.570 | 0.632 |
| 0.173 | 0.011 | 0.154 | 0.271 | 0.256 |
| 0.171 | 0.015 | 0.163 | 0.208 | 0.207 |
| 0.169 | 0.019 | 0.169 | 0.168 | 0.156 |
| 0.352 | 0.005 | 0.124 | 0.975 | 1.05 |
| 0.351 | 0.009 | 0.147 | 0.642 | 0.659 |
| 0.348 | 0.019 | 0.168 | 0.341 | 0.339 |
| 0.346 | 0.025 | 0.176 | 0.273 | 0.262 |
| 0.530 | 0.010 | 0.151 | 0.895 | 0.861 |
| 0.529 | 0.015 | 0.163 | 0.644 | 0.619 |
| 0.527 | 0.020 | 0.171 | 0.505 | 0.500 |
| 0.705 | 0.012 | 0.156 | 1.026 | 0.980 |
| 0.704 | 0.018 | 0.167 | 0.731 | 0.713 |
| 0.703 | 0.022 | 0.173 | 0.618 | 0.656 |
| 0.702 | 0.030 | 0.180 | 0.472 | 0.480 |
| Catalyst: 0 mol % $NdCl_3$, 400°C | | | | |
| 0.708 | 0.007 | 0.146 | 0.992 | 0.945 |
| 0.707 | 0.012 | 0.162 | 0.642 | 0.667 |
| 0.706 | 0.017 | 0.172 | 0.481 | 0.526 |
| 0.704 | 0.027 | 0.185 | 0.324 | 0.304 |
| 0.524 | 0.010 | 0.157 | 0.553 | 0.564 |
| 0.523 | 0.014 | 0.168 | 0.422 | 0.401 |
| 0.353 | 0.008 | 0.148 | 0.438 | 0.426 |
| 0.350 | 0.017 | 0.173 | 0.240 | 0.244 |
| 0.172 | 0.003 | 0.116 | 0.416 | 0.394 |
| 0.170 | 0.006 | 0.140 | 0.266 | 0.274 |
| 0.169 | 0.010 | 0.155 | 0.176 | 0.176 |
| 0.168 | 0.013 | 0.164 | 0.142 | 0.146 |
| 0.166 | 0.016 | 0.171 | 0.119 | 0.113 |

The equilibrium constant K_L does not depend on the concentration of neodymium chloride however, it is considerably dependent on temperature:

| | | | |
|-------|---------|--------|--------|
| °C | 380 | 400 | 420 |
| K_L | 0.00035 | 0.0007 | 0.0013 |

In Table I partial pressures of both chlorine and oxygen are given in atm, concentration of cupric chloride in mole fractions and the reaction rate has the dimension $\text{mol s}^{-1} \text{cm}^{-2}$.

Comparison of the calculated values of reaction rate with the experimental ones reveals clearly that the mentioned kinetic equation describes satisfactorily oxidation kinetics of hydrogen chloride oxidation with oxygen on catalysts of the chloride type, in the measured concentration range. This is a proof that the suggested mechanism is in accordance with the experimental data. The deviations of measured values from the calculated ones lie within the limits of possible errors with which the individual determinations are charged.

The main problem to be solved in the present work was to elucidate the promoting effect of admixture of alkali chlorides and rare earth chlorides to copper chlorides of the catalytically active substance. The reaction rate of catalytic oxidation of hydrogen chloride with oxygen is determined, as follows from the derived kinetic equation, by the rate of oxygen absorption in cuprous chloride. Since this absorption rate is strongly dependent on the content of potassium or neodymium chloride, the activity of the catalyst is also rather considerably influenced by admixture of the mentioned promoters to cuprous chloride.

Ruthven and Kenney⁵, in studying hydrogen chloride oxidation with oxygen, catalysed by melts based on copper chloride, employed the following kinetic equation

$$R = 4kj^2K^2a^2P_{O_2}/(jK + \sqrt{P_{Cl_2}})^2, \quad (5)$$

where k is the rate constant of oxygen absorption, j is the ratio of activity coefficients of copper chlorides, K is the equilibrium constant of the reaction $\text{CuCl}_2 = \text{CuCl} + 1/2 \text{Cl}_2$ and a is the overall concentration of copper chlorides.

Comparison of relations (4) and (5) reveals clearly that the dependence of the reaction rate on partial pressure of chlorine in (5) is somewhat more complicated. This is due to the different way of expressing the composition of the active mass. In Eq. (4) it is expressed in terms of cupric chloride concentration, whereas in Eq. (5) the total copper chloride concentration is used. By recalculating these expressions we can obtain comparable relations which, except for different formulation of the equilibrium constant, are identical. This means that the same relations are valid quantitatively for both hydrogen chloride oxidation, catalysed by melt surface, and by the active substance on a carrier. On the ground of this finding we can assume that with a carrier catalyst the effect of transport processes on the reaction rate is negligible.

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