Thermodynamic Modeling of ZnO Chlorination by Chlorohydrocarbons by Using «Astra» Software

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Abstract

The disposal and recycling of chlorohydrocarbons waste from organic synthesis which is annually produced at least 1,5 million tons is one of the global problems and is under the great UN's attention. Organochlorine residues are xenobiotics and adversely affect the environment. Thermodynamic modeling of interactions in the systems ZnO-CHxCly (x + y= 4)-O2 for determination of the theoretical content of chlorohydrocarbons as chlorinating agents for extracting nonferrous metals from very concentrated ore is presented in this article. The studies were conducted using the "Astra" software based on the principle of maximum entropy. Infobase of the "Astra" complex contains information on 5547 compounds, 79 items codified in the National Bureau of Standards and the Joint Institute for High Temperatures, Russian Academy of Sciences.

Introduction

Chlorine belongs to the products of chemical industry which necessity is steadily growing. In accordance with [1] the production of chlorine in 2005-2007 increased by 10,6% or 52 million tones. Chlorine-containing products grow proportionally to the production of chlorine.

An important problem in organochlorine synthesis is processing and using of organochlorine waste which formation in the world annually is at least 1,5 million tons [2]. The global nature of recycling organochlorine waste (OCW) is due to the fact that it belongs to xenobiotics (to be more exact to products having no analogous ones in nature) and so nature has no natural means to process them.

The main methods of OCW processing are thermooxidative incineration, pyrolysis, oxidation, chlorination, oxy-chlorination, chlorinoliz, biotechnology and electrochemical methods.

The purpose of this work is not the detailed analysis of methods of OCW processing. The global nature of the problem of OCW disposing is presented in [2, 3] in details. The method of high-temperature incinerations in furnaces of various designs (cyclone furnace, fluidized-bed furnace, plasma reactors) is the most used in practice. It should be noticed that this method is mastered by the following companies: Ude-Hehet, Niapon-Carbide, Nigtetd, Don-Poulenc, Yukari, Lurgi, Akzo, A-C-A, the Dow in the U.S., Japan, Germany, Holland, Italy, Australia [3]. The product of high-temperature combustion plants is hydrochloric acid or hydrogen chloride, which can be used in various industrial fields. To our best knowledge the chlorohydrocarbons can also be used for chloride-ferrous metals extraction from their oxides by combining combustion and chlorination. The purpose of this study is to analyze the effect of temperature and type of chlorohydrocarbons in the ranks of CHxCly (x+y=4) and C2HnClm (n+m=6) on the chlorination of ZnO-oxide being the basis of hard concentrated zinc-containing ores.

«Astra» software

In the first stage of research it was found that from a thermodynamic point of view chlorination of ZnO can be performed in a wide temperature

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range by different chlorohydrocarbons given in Table 1. This proves that in the presence of oxygen the thermodynamic probability of ZnO chlorination increases.

However the research of equilibrium of ZnO chlorination by Gibbs free energy (ΔG_T^0) does not make it possible to take into account being examined reactions. They are complex multicomponent systems. Thermodynamic analysis of systems by ΔG_T^0 is very difficult in computational nature because of the need for joint examining of all possible combinations of reactions in the system. The calculation of equilibrium for systems containing more than 5 compounds is practically impossible without special computer program [4]. In this connection, the second stage of the study was carried out using "Astra" software [5]. The algorithm is based on multipurpose «Astra» software using a universal thermodynamic method of determining the characteristics of equilibrium of arbitrary heterogeneous systems which is based on the fundamental principle of maximum entropy. The method allows finding the unique opportunity of a generalized description of any high-temperature state using only the laws of thermodynamics, regardless of the conditions and ways to achieve balance [6]. The advantage of the "Astra" complex is that it allows determining the equilibrium distribution of each element between the participants of the reactions and the composition of the gas phase at the interested temperature [7-9].

Table 1

Effect of temperature on Gibbs free energy (ΔG_T^0) of ZnO chlorination process

Reaction	ΔG_T^0, kJ / mol			
	673K	1273K	1573K	1873K
$3ZnO+2CHCl_3=3ZnCl_2+CO_2+H_2O$	-157,6	-287,6	-349,8	-410,2
$3ZnO+2CHCl_3+O_2= 3ZnCl_2+2CO_2+H_2O$	-307,1	-402,0	-447,2	-490,9
$5ZnO+2C_2HCl_5+2O_2= 5ZnCl_2+4CO_2+H_2O$	-360,2	-474,6	-529,4	-582,9

Results

Figure 1 shows the distribution of zinc in the systems $ZnO\text{-}CHCl_3$, $ZnO\text{-}CH_2Cl_2$, $ZnO\text{-}CH_3Cl$. The forecasting reactions were examined at that:

$$3ZnO+2CHCl_3+O_2=3ZnCl_2+2CO_2+H_2O \quad (1)$$

$$ZnO+CH_2Cl_2+O_2= ZnCl_2+CO_2+H_2O \quad (2)$$

$$ZnO+2CH_3Cl+3O_2= ZnCl_2+2CO_2+3H_2O \quad (3)$$

In these systems depending on the temperature 15 elements and compounds are involved in the interaction (ZnO, $CHCl_3$, O_2, O, H_2, H, H_2O, Cl_2, Cl, HOCl, CO, CO_2, $ZnCl_2$, ZnCl, Zn). Calculations show that in systems regardless of the type of chlorohydrocarbons the zinc at temperature of 300K is completely chlorinated. Then with increasing temperature a secondary zinc oxide begins to form with a simultaneous increasing the degree of transformation of Zn into the gaseous $ZnCl_2$. To determine the reasons of the formation of secondary ZnO we have also researched the distribution of Cl, O and N. On the basis of which we have obtained chemical equations, for example for the system $ZnO\text{-}CHCl_3$.

<u>T=300K</u>

$$3ZnO+2CHCl_3+O_2= 3ZnCl_2+2CO_2+H_2O \quad (4)$$

<u>T=1000K</u>

$$3ZnCl_2+2CO_2+H_2O=2{,}658ZnCl_2+0{,}342ZnO+2CO_2 + 0{,}372H_2O+0{,}256HCl+0{,}0089Cl_2+0{,}0325O_2 \quad (5)$$

Thus the formation of secondary ZnO is due to the interaction of $ZnCl_2$ with H_2O. The interaction is similar for example in the system $ZnO\text{-}CH_3Cl\text{-}O_2$ characterized by a greater degree of ZnO formation (28,5% at T=900K):

<u>T=300K</u>

$$ZnO+2CH_3Cl+3O_2= 3ZnCl_2+2CO_2+3H_2O \quad (6)$$

<u>T=900K</u>

$$3ZnCl_2+2CO_2+3H_2O=0{,}715ZnCl_2+0{,}285ZnO + +2C_2+2{,}715H_2O+0{,}57HCl \quad (7)$$

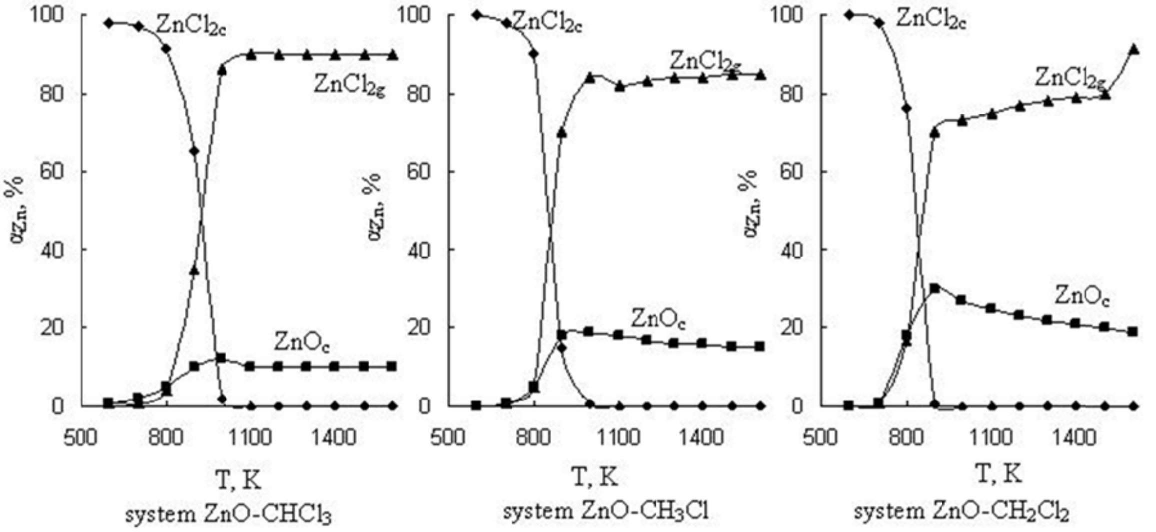

Fig. 1. The action of temperature on the degree distribution of zinc in the systems ZnO- $C_2H_xCl_y$ (x+y = 4) at a pressure of 0,1 MPa

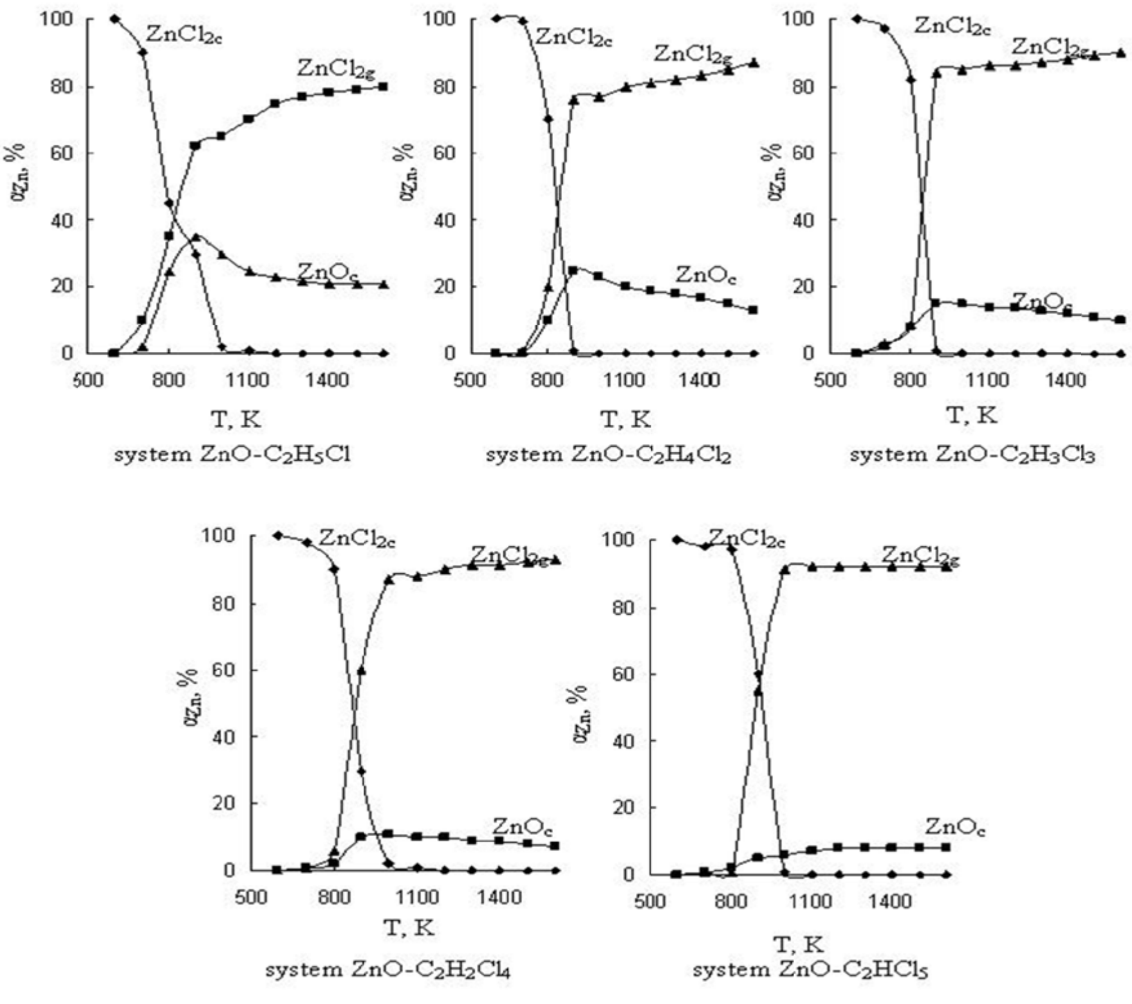

Fig. 2. The action of temperature on the degree distribution of zinc in the systems $C_2H_nCl_m$ (n+m=6) at a pressure of 01 MPa

Figure 2 provides information of the effect of temperature on the behavior of zinc using chlorohydrocarbons group $C_2H_nCl_m$ (n+m=6), which proves that the chlorination in the system is also complicated by the formation of secondary ZnO, in which, for example in the system ZnO-C_2H_5Cl-O_2, passes 35,5% Zn at T = 900K. This process equation has the form:

T=300K

$$ZnO+2C_2H_5Cl+6O_2=ZnCl_2+4CO_2+5H_2O \quad (8)$$

T=900K

$$ZnCl_2+4CO_2+5H_2O=0{,}645ZnCl_2+0{,}355ZnO+4CO_2+4{,}645H_2O+0{,}71HCl \quad (9)$$

Increasing of the temperature up to 1600K results in decrease in the transition of zinc into ZnO and in increase in the transition into $ZnCl_2$. Thus at T = 1600K the process is described by the equation:

$$0{,}645ZnCl_2+0{,}355ZnO+4CO_2+4{,}645H_2O+0{,}71HCl=0{,}758ZnCl_2+0{,}241ZnO+0{,}008Zn+4CO_2+4{,}76H_2O+0{,}48HCl. \quad (10)$$

The examined chlorohydrocarbons contain chlorinating (Cl) and recovering (C and H) components. Obviously the ratio of these elements can influence the behavioral pattern of Zn. Therefore we have chosen the ratio of chlorine atoms to the amount of hydrogen and carbon in chlorohydrocarbons, i.e. Cl/(H+C)=θ. Table 2 and Figures 3 show the effect of θ on the temperature of onset of ZnO formation (ZnO T_o, R), the maximum degree of transformation into secondary ZnO Zn (α_{max}ZnO, K) and the degree of transformation of Zn into the gaseous zinc chloride (α_{ZnCl2},%).

Table 2 and figure 3 show that the increase of θ leads to an increase of T_oZnO, α_{ZnCl2} and to reduce of α_{max} ZnO in accordance with the equations:

$$T_oZnO=685{,}82+70{,}796\cdot \ln \theta \ (R^2=0{,}9726) \quad (11)$$

$$T_{max}ZnO=12{,}488-11{,}097\cdot \ln \theta \ (R^2=0{,}9634) \quad (12)$$

$$\alpha_{ZnCl2}=91{,}885+7{,}9287\cdot \ln \theta \ (R^2=0{,}9821) \quad (13)$$

Table 2

Effect of parameter θ chlorohydrocarbons on T_N ZnO, α_{max}ZnO, α_{ZnCl2}

Parameter	Chlorohydrocarbons							
	C_2HCl_5 θ=1,666	$CHCl_3$ θ =1,5	$C_2H_2Cl_4$ θ =1,0	CH_3Cl_2 θ=0,666	$C_2H_3Cl_3$ θ =0,6	$C_2H_4Cl_2$ θ =0,33	CH_3Cl θ =0,25	C_2H_5Cl θ=0,143
T_nZnO,K*	738	709	689	647	635	607	599	549
α_{max}ZnO,%	6,4	11,8	10,6	15,8	16,9	23,7	28,6	35,5
α_{ZnCl2},%	95,1	90,9	91,8	89,0	88,5	84,9	80,4	75,3

*- In our case the temperature of onset of ZnO formation is the temperature at which the degree of formation of secondary ZnO is 1%.

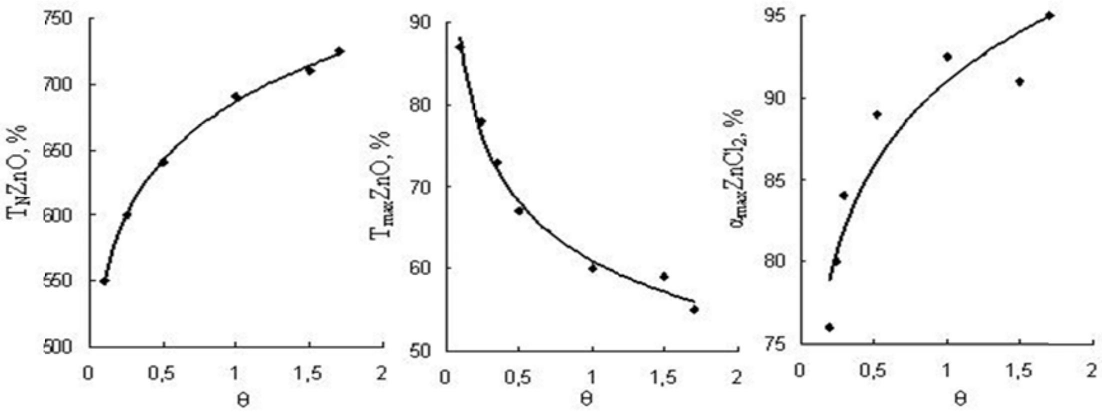

Fig. 3. The action of θ T_NZnO, $\alpha_{max}ZnCl_2$ of zinc in the systems $C_2H_nCl_m$ (n+m=6) at a pressure of 0,1 MPa

Effect of pressure on the behavior of zinc was determined in the systems $ZnO\text{-}CH_xCl_y$ (x+y=4). It is seen from the Figures 4,5 that decrease of the pressure leads to increases of the degree of secondary ZnO formation and transition of Zn into the gaseous element state at T>1400K. The main components of the gas phase are $ZnCl_2$, CO_2, H_2O, HCl, Zn (Figure 6). Gas phase system $ZnO\text{-}CHCl_3\text{-}O_2$, for example, at 1600K and P=0,1 MPa, has the following composition, volume %: 46,44 $ZnCl_2$, 33,09 CO_2, 13,39 H_2O, 6,31 HCl, 0,008 CO, 0,025 Zn, 0,005 Cl_2, 0,62 O_2, 0,08 Cl, 0,001 H_2.

Based on the data presented in the figures the equation of pressure effects on $T_{max}ZnO$ is identified:

$$T_{max}ZnO\ (\text{for } CHCl_3)=10,167-1,15 \cdot \lg P \quad (R^2=0,9845) \qquad (14)$$

$$T_{max}ZnO\ (\text{for } CH_2Cl_2)=14,1-2,25 \cdot \lg P \quad (R^2=0,848) \qquad (15)$$

$$T_{max}ZnO\ (\text{for } CH_3Cl)=23.07-5.1 \cdot \lg P \quad (R^2=0,9873) \qquad (16)$$

Giving the possibility of such chlorohydrocarbons by θ we show the generalized dependence of $T_{max}ZnO = f(\theta, P)$:

$$T_{max}ZnO=12,416-7,239 \cdot \ln\theta - (1,8038-2,2288 \cdot \ln\theta) \cdot \lg P \qquad (17)$$

$$T_{max}ZnO=24,461 \cdot \exp[-0,6166 \cdot \theta]-5,9042 \cdot \exp[-1,1365 \cdot \theta] \cdot \lg P \qquad (18)$$

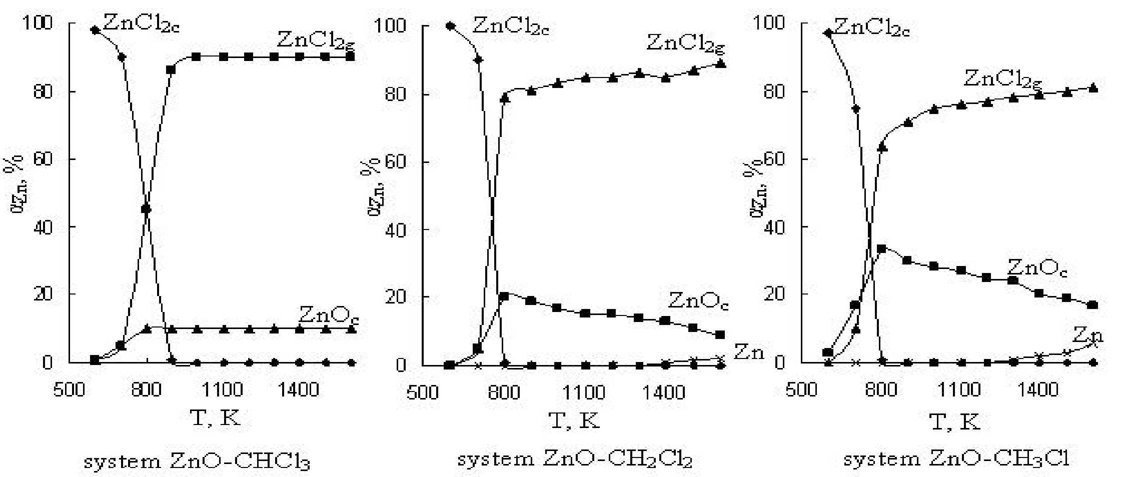

Fig.4. The action of temperature and pressure (0,01 MPa) on the degree distribution of zinc in the systems $ZnO\text{-}C_2H_xCl_y$ (x+y = 4)

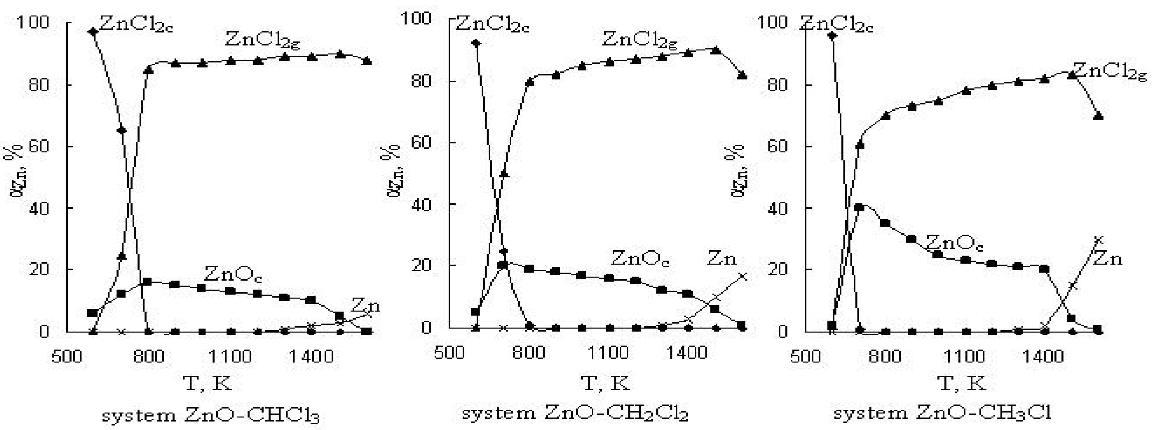

Fig.5. The action of temperature and pressure (0,001 MPa) on the degree distribution of zinc in the systems $ZnO\text{-}C_2H_xCl_y$ (x+y = 4)

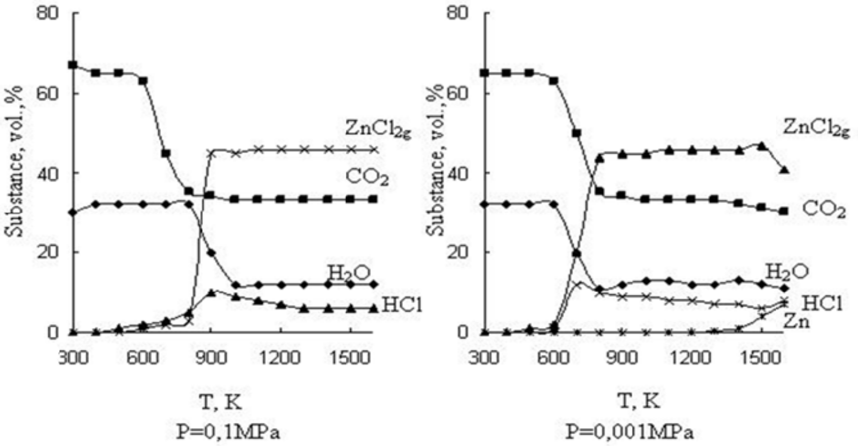

Fig. 6. The action of temperature and pressure (P) on the gas phase composition of systems $ZnO\text{-}CHCl_3\text{-}O_2$

Conclusion

Researches of thermodynamic modeling of interactions in the systems ZnO-chlorohydrocarbons [CH_xCl_y (x+y=4) и $C_2H_nCl_m$ (n+m=6)- O_2] revealed that:

- regardless of the type of chlorohydrocarbons in the systems at T=300K condensed zinc chloride, water and carbon monoxide (IV) are formed;
- in the systems we observe the formation of secondary ZnO due to the interaction of $ZnCl_2$ with H_2O;
- the influence of the type of chlorohydrocarbons on equilibrium distribution of zinc in these systems is determined by the ratio of Cl/(H+C) in chlorohydrocarbons;
- increasing the ratio of Cl/(H+C) in chlorohydrocarbons from 0,143 (C_2H_5Cl) to 1,667 (C_2HCl_5) increases the temperature of the onset of formation of ZnO from 549 to 738K, and reduces the maximum degree of formation of ZnO from 35,5% (C_2H_5Cl) to 6,4% (C_2HCl_5);
- maximum degree of Zn chloridation depends on the ratio Cl/(H+C) in chlorohydrocarbons, increasing from 75,3% to 95,1% with increase of the ratio Cl/ (H +C) from 0,143 to 1,667;
- reduction of pressure in the systems $ZnO\text{-}CH_xCl_y$ (x+y=4) increases the temperature of maximum formation of ZnO according to the equation $T_{max}ZnO = A\text{-}B \cdot lgP$.

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Received 15 October 2009.