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TG STUDIES ON THE REACTIONS OF HEMATITE, MAGNETITE AND WUSTITE WITH CCl_4

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ABSTRACT

The chlorination of hematite, magnetite and wustite with gaseous CCl_4 were studied by thermogravimetry. The equilibrium compositions of the gas- and solid phases were determined by computer assisted thermodynamic calculations. In the case of hematite a reaction order of 0.5 was found with an apparent activation energy of 125 $kJ.mol^{-1}$. During the chlorination of wustite solid $FeCl_2$/s/ was detected as intermediate product. A simultaneous transformation of wustite was observed, first into magnetite, at higher temperatures, into hematite. Similarly, $FeCl_2$ and hematite were formed as intermediate products during the chlorination of magnetite. Temperature and partial pressure dependence of the $FeCl_2$/s/ formation and volatilization were also studied.

INTRODUCTION

Chlorination behaviour of iron oxides were studied in some recent publications /refs. 1-3/. The reaction of iron oxides with chlorine has been investigated by us /ref.4/ in order to obtain additional thermodynamic and kinetic data for Fe-O-Cl system. The present paper as an extension of this work deals with the reactions between Fe_2O_3, Fe_3O_4, FeO and gaseous CCl_4 in the temperature range 3oo-12oo K at 0.5-10 kPa CCl_4 partial pressures.

EXPERIMENTAL

TG measurements were carried out in a special reactor attached to a METTLER semimicro recording balance /ref.5/. Ferric oxide of analytical grade /s^o = 10 $m^2.g^{-1}$/ was used. Wustite samples were prepared from iron oxalate by thermal decomposition /s^o = 0.4 $m^2.g^{-1}$/ and magnetite from ferric oxide by reduction /s^o = 0.3 $m^2.g^{-1}$/. The crystalline structure of the samples were checked by X-ray diffraction.

RESULTS AND DISCUSSION

The gas- and solid-phase equilibria in the $FeO+CCl_4$ system were determined by a computer assisted free-enthalpy minimalization program. The temperature dependence of the equilibrium composition is strongly effected by the ratio of

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FeO:CCl$_4$. In the case of 5:1 ratio the predominant gas product is CO$_2$, while Fe$_3$O$_4$, FeCl$_2$ and C can be found in the solid phase /Fig.1A/. In the case of 2:1 mole ratio the solid phase is completely transformed into FeCl$_2$ /Fig.1B/. Increasing the proportion of CCl$_4$, FeCl$_3$/s/ appears in the solid phase under 500 K, while the Fe$_2$Cl$_6$/g/ will be the predominant gasproduct above 500 K.

The chlorination processes were characterized by anisothermal TG measurements /Fig.2A/. In the case of hematite the volatilization was not preceeded by mass gain. The temperature dependence of the chlorination rate was studied by isothermal TG measurements /Fig.3A/. The local maximum of the reaction rate /R$_0$/ at 900 K is caused by the thermal decomposition of CCl$_4$. An apparent activation energy of 125 kJ.mol^{-1} was obtained in the temperature range 670-870 K. A reaction order of about 0.5 was found from the partial pressure dependence of the chlorination rate /Fig.3B/.

During the anisothermal chlorination of wustite /Fig.2A, curve 2/ the two mass gain steps can be explained by the formation of solid FeCl$_2$/s/ and the simultaneous transformation of wustite first into magnetite and at higher temperatures into hematite. Volatilization of FeCl$_2$ in form of Fe$_2$Cl$_6$/g/ causes a rapid mass loss in the anisothermal TG curve at about 750 K, followed by slow volatilization attributed to the hematite + CCl$_4$ reaction. Similarly, FeCl$_2$/s/ and hematite are formed as intermediate products during the reaction of magnetite with CCl$_4$ /Fig.2, curve 3/. This was proved by X-ray diffraction analysis:

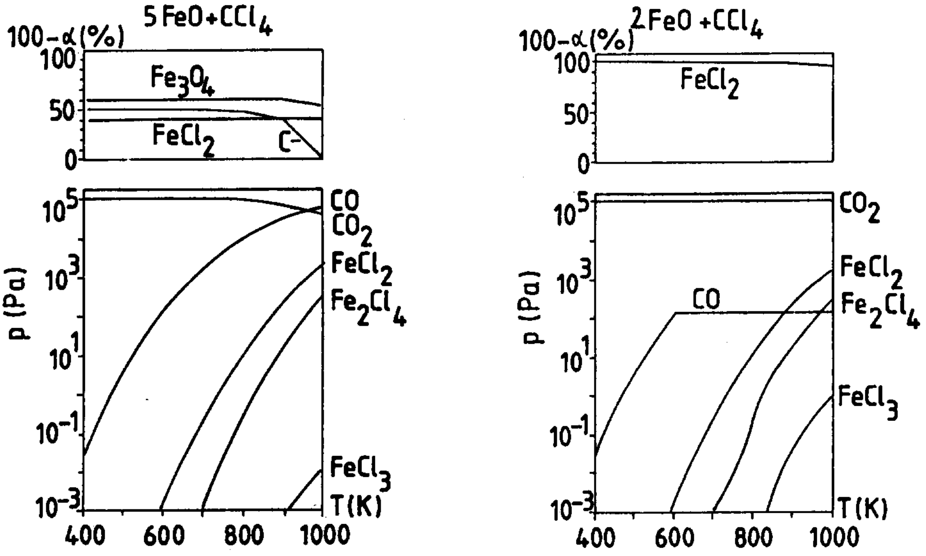

Fig.1. Temperature dependence of the concentrations of the solid and gaseous products in the system FeO-CCl$_4$ at p=10^5 Pa./A/ FeO:CCl$_4$=5:1 /B/ FeO:CCl$_4$=2:1

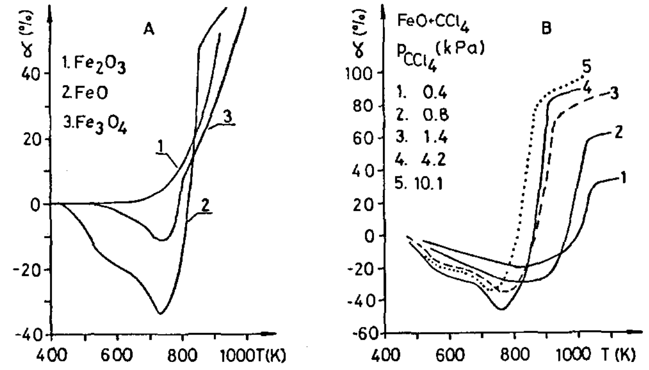

Fig.2. /A/ Anisothermal TG curves, p_{CCl_4}=2.1 kPa. /B/ partial pressure dependence of the anisothermal TG curves in the case of the chlorination of FeO. Heating rate: 10 K.min^{-1}, α: mass loss

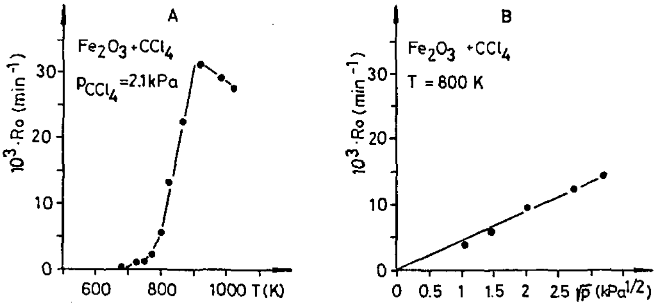

Fig.3. Temperature and partial pressure dependence of the reaction rate in the case of the chlorination of Fe_2O_3

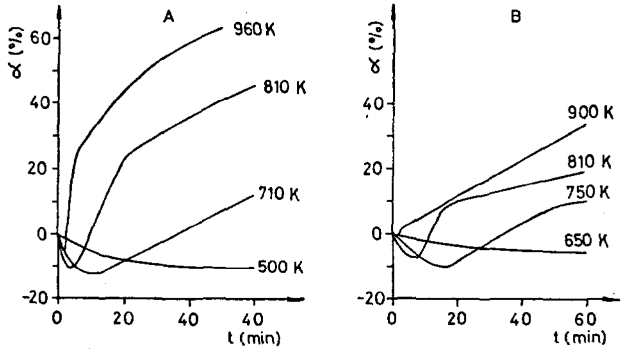

Fig.4. Isothermal chlorination measurements at p_{CCl_4}=2.1 kPa. /A/-FeO; /B/-Fe_3O_4

magnetite was detected in the solid phase, when the anisothermal chlorination of wustite was interrupted at 600K, while magnetite+hematite were found at 750K. And nearly the whole solid phase was transformed into hematite during the isothermal chlorination at 750 K.

The partial pressure dependence of the anisothermal chlorination of FeO is seen in Fig.2B. The highest mass change was observed at 4.2 kPa CCl_4. The conversion values at 600 K correspond to the mass gain caused by the complete transformation of the wustite into magnetite and at 750 K to hematite at a simultaneous formation of $FeCl_2$/s/ /27 %, 46 % resp./. As the volatilization rate of the gaseous products is also increased with CCl_4 concentration, mass gain steps are decreased at pressure above 4.2 kPa.

Characteristic isotherms of FeO and Fe_3O_4 are seen in Fig.4. At lower temperatures only mass gain can be observed due to the formation of $FeCl_2$/s/. Increasing of the reaction temperature results in the volatilization of $FeCl_2$ in form of Fe_2Cl_6/g/. After an initial mass gain step two volatilization region can be distinguished in the isothermal curves above 750 K attributed predominantly to the volatilization of $FeCl_2$ and to the chlorination of hematite. At higher temperatures /T>900 K/ the formation and the volatilization of $FeCl_2$ is very fast.

The following overall chemical equations are proposed for describing the above chlorination processes:

$$4\,FeO/s/ + 1/2\,CCl_4/g/ = Fe_3O_4/s/ + FeCl_2/s/ + 1/2\,C/s/ \qquad /1/$$

$$4\,FeO/s/ + CCl_4/g/ = Fe_2O_3/s/ + 2\,FeCl_2/s/ + 1/2\,C/s/ + 1/2\,CO_2/g/ \qquad /2/$$

$$Fe_3O_4/s/ + 1/2\,CCl_4/g/ = Fe_2O_3/s/ + FeCl_2/s/ + 1/2\,CO_2/g/ \qquad /3/$$

$$FeCl_2/s/ + 1/2\,CCl_4/g/ = 1/2\,Fe_2Cl_6/g/ + 1/4\,C_2Cl_4/g/ \qquad /4/$$

$$Fe_2O_3/s/ + 3/2\,CCl_4/g/ = Fe_2Cl_6/g/ + 3/2\,CO_2/g/ \qquad /5/$$

The results of the TG and X-ray measurements and of the thermodynamic calculations are consistent with these simplified equations.

REFERENCES

1 D.Neuschütz, E.Mann and O.Knacke, Erzmetall, 30 /1977/ 464

2 R.Titi-Manyaka and I.Iwasaki, Trans., AIME, 252 /1972/ 307

3 R.J.Freuhan, L.J.Martonik, Met. Trans. 4 /1973/ 2793

4 V.I.Evdokimov, I.Z.Babievskaja, N.F.Drobot, I.Bertóti, T.Székely and I.S.Pap, Zh. Neorg. Khim., to be published

5 I.Bertóti, A.Tóth, I.S.Pap and T.Székely, Therm.Anal., ICTA 80, Birkhäuser Verlag, Basel, Boston, Stutgart, 1980, Vol. 2.p. 235