



THERMODYNAMICAL ANALYSIS OF (Fe-O-Cl) SYSTEM

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Abstract: Today, the control and the regulation of the processes of metalurgy of metal extraction, or other kind of their chemical thermal treatment, should be based on previously well studied and defined parameters for efficient work.

While projecting new technologies or optimizing the existing ones, the scientific approach is based on the treatment of an enormous number of information and data.

The chemical thermodynamics with the previous thermodynamical analysis also has a great part in this. Most often it's all about complex systems, making analysis applying the classical method assumes great work, yet the results derived from the analysis are not always clearly visible.

In this scientific work, based on literature data for the necessary thermodynamical values, a thermodynamical analysis was made on the system Fe-O-Cl.

When making the analysis, the program "THERMANAL" specialized on the Institute of Extractive Metalurgy (TMF-Skopje) was used as software.

With this analysis, the areas of stability of pure condensed phases in the system Fe-O-Cl, are defined, depending on the potential of the gas species at a constant temperature of 833 and 881 K, and the results are given graphically in the plain $\log P_{Cl_2} [bar] - \log P_{O_2} [bar]$ and the Gibbs triangle of concentrations.

INTRODUCTION

It is known that during etching process of thin steel strips with hydrochloric acid in rolling mills it is derived a dissolution rich with iron chlorides and a small amount of other metals.

During regeneration process of hydrochloric acid by high temperature hydrolysis of iron chloride ($FeCl_2$) according to



it is derived a fine disperse Fe_2O_3 dust and a insignificant quantity of chlorides and oxichlorides of other metals in condensed condition.

From the great number of ways to valorize this quality raw material from a metalurgic aspect, it was decided to study the process of low temperature reduction with hydrogen leading to chemically clean and active iron powder.

During the parameters composing that open a possibility of defining of all segments of the reduction process derived from the existing goal in this ease is also:

- previous thermodynamical analysis of the condition in the Fe-O-Cl system i.e. determination of the thermodynamical stability of the condensed phases depending on the composition of the gas phase.

SYSTEM Fe-O-Cl

The condition of the condensed phases αFe , $FeCl_2$, αFe_2O_3 , Fe_3O_4 will be analyzed here, using thermodynamical calculations based on literature data [1,2,3] added in table (1).

For $T > 600$ K, the substance $FeCl_3$ is stable only in gas condition ($P_{FeCl_3} > P^o$). In this system, equilibrium condition is a function of three intensive values: P_{O_2} , P_{Cl_2} and T . If we use one extent of liberty, for example $T = const.$, then with $B=1$ [4] in the equation

$$F = K - P - B + 2 \quad (2)$$



we can determine the variance of the equilibrium conditions in this system in the $\log P_{Cl_2} - \log P_{O_2}$ plain. In the equation (2) the number of components K is to be calculated from the number of substances and the number of linear independent chemical reactions R or

$$K = S - R \tag{3}$$

For example, the coexistence of the condensed phases $FeCl_2/Fe_3O_4$, is given with the chemical reaction:



first the variance of the coexistence of these two phases should be determined:

- S=4; $FeCl_2, Fe_3O_4, O_2, Cl_2$
- R=1; chemical reaction (4)
- P=3; two condensed phases $FeCl_2, Fe_3O_4$ and one gas phase mixture (O_2-Cl_2)
- B=1; condition $T=const.$

The equation (3) derives $K=3$, and successively from the equation (2) the system is monovariant ($F=1$). The position of this coexistence line for $T=const$ in the $\log P_{Cl_2} - \log P_{O_2}$ plain is determined by the equation for K_p of the chemical reaction (4)

$$K_p(4) = P_{Cl_2}^3 \cdot P_{O_2}^{-2}$$

$$\log P_{Cl_2} = 1/3 \log K_p(4) + 2/3 \log P_{O_2} \tag{5}$$

For $F=1$, the equilibrical condition, i.e. the coexistence of the condensed phases $FeCl_2$ and Fe_3O_4 , can be moved at any point of the coexistence line determined with the equation (5) through an arbitrary variation of only one intensive value: P_{O_2} or P_{Cl_2} .

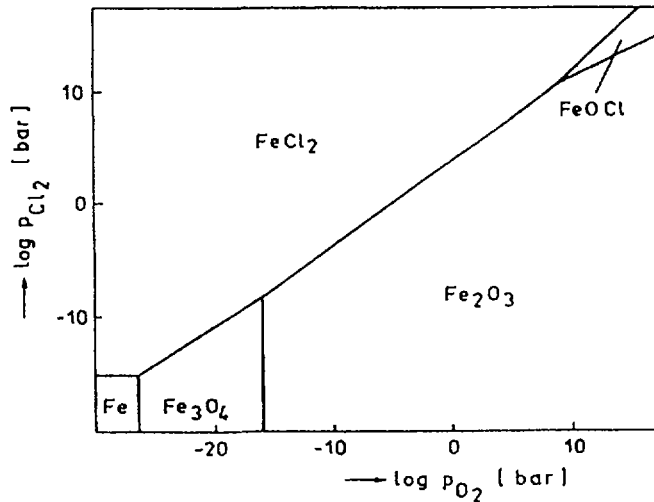
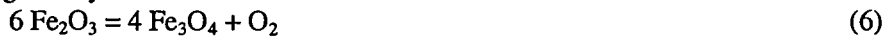


Figure 1. Phase diagram of the system Fe-O-Cl at $T=833$ K

Variance of the coexistence of the condensed phases Fe_3O_4 and Fe_2O_3 will be determined. This coexistence is given by the chemical reaction



For this equivalence follows that

- S=3; Fe_2O_3, Fe_3O_4, O_2
- R=1; chemical reaction (6)
- P=3; two condensed phases and one gas phase
- B=1; condition $T=const$



From equation (3) $K=2$, so applied in the chemical reaction (6) $F=0$ – nonvariant condition is completed. This means that the equilibrium condition is determined only by the intensive values P_{O_2} and T . This is because Cl_2 does not participate in the chemical reaction (6). For constant temperature, position of P_{O_2} in the plain $\log P_{Cl_2} - \log P_{O_2}$ is exactly determined by the temperature:

$$\log P_{O_2} = \log Kp(6) = \text{const.} \tag{7}$$

The position of the coexisting line in the previous equation is independent from the variation of P_{Cl_2}

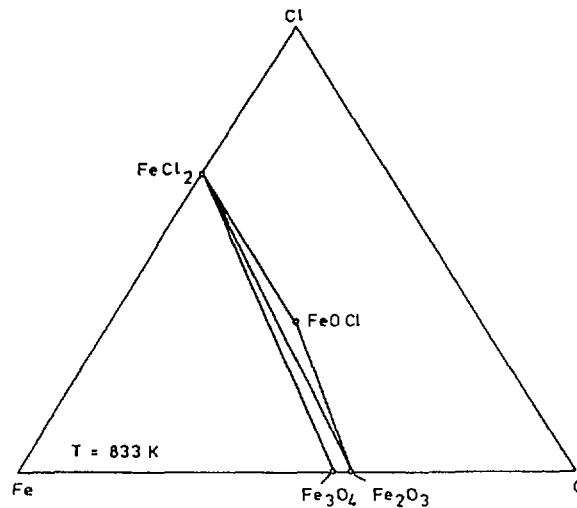


Figure 2. Gibbs concentration triangle of the system Fe-O-Cl at T=833 K

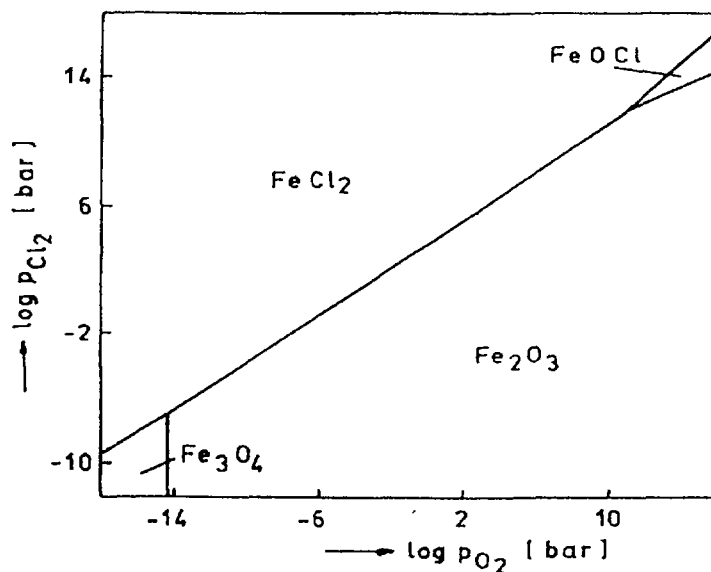


Figure 3. Phase diagram of the system Fe-O-Cl at T=881 K

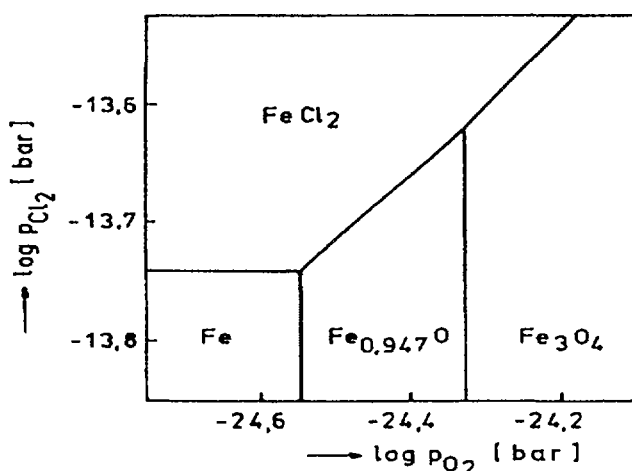


Figure 4. Phase diagram of the system Fe-O-Cl at T=881 K

By the same procedure can be proved that the coexistence of condensed phases Fe/FeCl₂, given with the chemical reaction



for $T=\text{const.}$ represents a nonvariant condition. The position of the coexisting line for this equality in the plain $\log P_{\text{Cl}_2} - \log P_{\text{O}_2}$ is exactly determined by the temperature:

$$\log P_{\text{Cl}_2} = \log Kp(8) = \text{const} \quad (9)$$

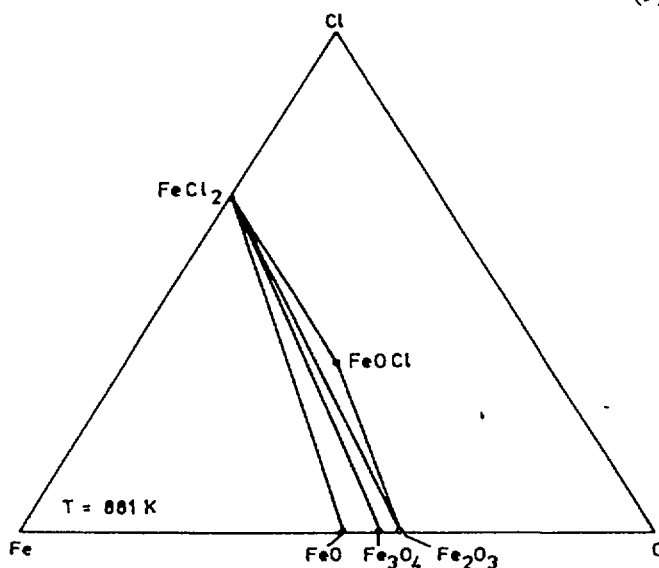


Figure 5. Gibb's concentration triangle of the system Fe-O-Cl at T=881 K

For a system of six ($n=6$) condensed phases according to equation $m = \binom{n}{2}$, maximal number of coexisting lines m is 15 (equality of two condensed phases), while from equation $l = \binom{n}{3}$ maximal number of possible triple points l (coexistence of three condensed phases in same point in the plain $\log P_{\text{Cl}_2} - \log P_{\text{O}_2}$ for $T=\text{const.}$) is calculated to be 20.



Implementation of the classical method for determination of stability areas of condensed phases (pure substances) in the plain $\log P_{Cl_2} - \log P_{O_2}$ at $T=\text{const}$ is practically inapplicable because of the size of that calculation procedure in this system with 15 possible coexistence lines and 20 possible triple points. The graphic-analytical method suggested by I. Barin [5] gives a good view and essentially reduces the procedure of analytic calculations for systems with lower number of coexisting lines and triple points. Yet, for an analysis of this system, this method requires a large calculation procedure.

Today, from this reasons, a commercial software systems with a thermodynamical database built inside, are used for this kind of analysis. The analysis of the system Fe-O-Cl for $T=833$ K and $T=881$ K in this scientific work was made by thermodynamical data presented in table (1) and with the aid of software program "THERMANAL" [6].

Results of the thermodynamical analysis are graphically presented on pictures (1, 2, 3, 4 and 5). From the phase diagrams, presented on previous pictures, it's visible that the coexistence of $FeCl_2$ with Fe-oxides Fe_xO_y , is thermodynamically stable. At the same time, it is remarkable that with oxidation of $FeCl_2$ with oxygen gas, at given temperature and composition of the gas phase, the quantity of $FeCl_2$ that has not been oxidized yet is thermodynamically stable on the limit with derived Fe-oxide or oxichloride. In other words, the coexistence of $FeCl_2$ with other condensed phases of this system is thermodynamically stable.

Table 1. Literature thermodynamical data of standard forming enthalpy, standard entrophy, molar heat capacity and the change of phase transformation enthalpy

substance	ΔH° (298) kJ/mol	S° (298) J/mol K	$C_p = a + bT + cT^{-2}$ J/mol K			Interval T [K]	Reference
			a	b 10^3	c 10^{-5}		
Fe (α)		27.154	17.489	27.769		273 - 1033	[2]
$Fe_{0.947}O$	- 266.270	57.589	48.785	8.368	- 2.803	298 - 1650	[2]
Fe_3O_4	- 1118.385	146.440	86.266	208.916		298 - 866	[2]
Fe_3O_4 transformation (α/β) at 866 K $\Delta H^\circ = 0$							[2]
Fe_3O_4 (β)			200.832			866 - 1870	[2]
Fe_2O_3 (α)	- 825.503	87.466	98.282	77.822	- 14.853	298 - 953	[1]
$FeCl_2$	- 342.251	117.989	79.245	8.703	- 4.895	298 - 950	[1]
$FeOCl$	- 408.568	76.567					[1]
O_2 (g)		205.037	29.957	4.181	- 1.674	298 - 3000	[2]
Cl_2 (g)		222.965	36.903	0.2510	- 2.845	298 - 3000	[1]
HCl (g)	- 92.312	186.786	26.527	4.602	1.088	298 - 2000	[1]

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