

# Thermodynamic Analysis Of Chalcopyrite Oxidation-Reduction Process

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**Abstract**— The only reactions that occur during melting with heat release are the reactions of oxidation of the components of the raw material with oxygen. During the processing of sulfide ore raw materials, the main exothermic reactions that provide sufficient heat release for the autogenous process are sulfide oxidation reactions. Thus, all autogenous metallurgical processes, being oxidative, require the supply of an oxygen-containing blast. The most widely used at present autogenous melting processes according to the method of oxidation of charge sulfides can be divided into two groups. In the processes of the first group, the combustion of sulfides is carried out in an oxygen or air-oxygen flare (suspended (WP) or Finnish, oxygen-flare smelting (CFP), kivetset process); In the processes of the second group, the oxidation of charge sulfides is carried out directly in the melt. A number of varieties of these processes are in commercial operation: the Vanyukov smelting (PV), the Noranda, Mitsubishi, Bai-Yun processes, and smelting in converters. The structure of the heat balance of autogenous melting depends on the composition of the feedstock obtained during the melting of matte and slag, the oxygen content in the blast and temperature. The higher the heat input, the more sulfur is contained in the raw material, the higher the content of non-ferrous metals in the resulting matte, and the higher the blast temperature. The heat consumption is mainly associated with heat losses from the smelting products, especially from gases. With an increase in the oxygen content in the blast, heat losses with gases are noticeably reduced due to a decrease in the nitrogen content in them, and hence the total volume of exhaust gases. All autogenous melting processes have characteristic features. Some proceed with the use of oxygen blast (CFP), others - with oxygen-enriched blast (flash melting - VP, melting Vanyukov - PV). In the process of flash melting, the blast is usually also heated. When melting, by adjusting the desulfurization, it is possible to obtain mattes with a high content of non-ferrous metals - copper or nickel. Modern processes of autogenous melting can be carried out not only on rich mattes, but also on white matte, matte and even blister copper.

**Keywords**— metallurgy, copper, chalcopyrite, oxidation, reduction, processing, thermodynamic changes.

Chalcopyrite (Greek Chalkos copper and pyrite), copper pyrite - mineral, copper and iron sulfide. The chemical composition is CuFeS<sub>2</sub> (34.57% copper, 30.54% iron, 34.9% sulfur), without a mixture of Ag, Zn, Au, As, Se, Sn. Crystallizes in tetragonal and cubic syngonium. Mort. Semiconductor; antiferromagnetic. Donator forms latent crystalline, sometimes kidney-like aggregates. The color is golden yellow, orange. Shiny as metal. Hardness 3-4; density 4.1-4.3 g / cm<sup>3</sup>. It occurs in almost all genetic types, from igneous deposits to sedimentary deposits. Misnickel sulfide deposits located between intrusive rocks are found along with pyrrhotite, pentlandite, magnetite, cubanite, and other minerals. During erosion, cuprite, malachite, limonite, chrysocolla and other minerals are formed due to X. X. is the most common mineral of copper and the main mineral of copper ores. The deposits are located in the Russian Federation (Norilsk), Kazakhstan (Jezkazgan), Canada, Spain, Great Britain, the USA and Central Africa. It is found in Almalyk, Kungrad, Korgoshinkon, Kalmakkir, Koshbulak, Karamazor deposits in Uzbekistan. Several studies have shown that oxidizing chalcopyrite to oxidizing compounds [1-15].



The thermodynamic values of the starting materials are given in Table 1.

**Table 1.** Appropriate thermodynamic quantities of substances (298 K)

Substance	CuFeS <sub>2</sub>	O <sub>2</sub>	Cu <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	SO <sub>2</sub>
$\Delta H$ (kJ/mol)	-188.3	0	-173.2	-822	-296.9
$\Delta G$ (kJ/mol)	-194.1	0	-150.6	-740	-300.21
$\Delta S$ (J/(mol*K))	143.8	205.04	92.9	87	248.07

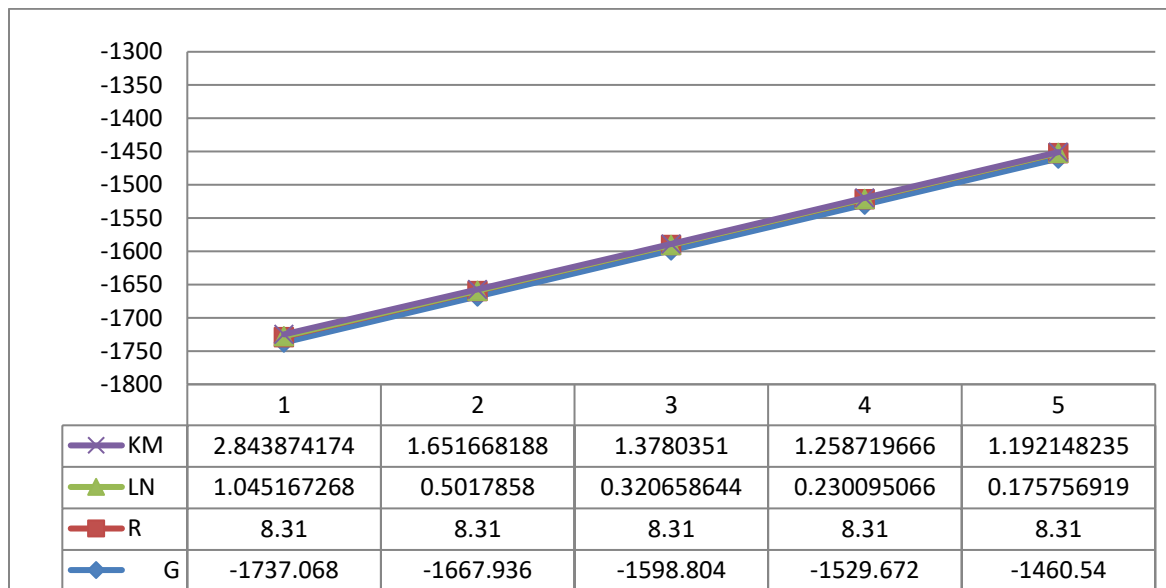
$$\Delta H_{\text{Reaction}}^{298} = -1806.2 \text{ kJ}; \Delta G_{\text{Reaction}}^{298} = -1703.24 \text{ kJ}; \Delta S_{\text{Reaction}}^{298} = -345.66 \text{ kJ}$$

From the results under standard conditions, it can be seen that the enthalpy value of the reaction is negative (exothermic), ie the reaction produces heat. Although the value of the free energy of the reaction is also secret, it is necessary for the substances to provide the appropriate activation energy for the chemical reaction to take place [16-23]. The values of the equilibrium constant

from the Gibbs energy values are shown in Table 2 and in the diagram, as well as how the increase in temperature affects the reaction rate after the onset of the interaction of substances in the system:

**Table 2.** Results of thermodynamic analysis of oxidation of chalcopyrite mineral

$\Delta H$	$\Delta S$	T	$\Delta G$	R	$\ln K_M$	$K_M$
-1806,2	-0,346	200	-1737,07	8,31	1,045167	2,843874
-1806,2	-0,346	400	-1667,94	8,31	0,501786	1,651668
-1806,2	-0,346	600	-1598,8	8,31	0,320659	1,378035
-1806,2	-0,346	800	-1529,67	8,31	0,230095	1,25872
-1806,2	-0,346	1000	-1460,54	8,31	0,175757	1,192148

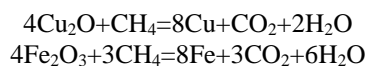


**Figure 1.** Temperature dependence diagram of oxidation kinetics of chalcopyrite mineral

When studying the thermodynamic possibilities of oxidation of chalcopyrite with a large amount of oxygen, it was found that at a temperature of 800 °C (1000 K) the equilibrium in the chemical reaction shifts to the right, ie to the product formation side.

Let's look at the process of reduction of metal oxides with methane [24-26].

The reduction of copper oxide and iron oxides with methane allows the production of pure copper and iron metals. The chemical reaction that takes place during the recovery process is as follows:



The thermodynamic values of the obtained substances are given in Tables 3-4.

**Table 3.** Appropriate thermodynamic quantities of substances (298 K)

Substance	$\text{Cu}_2\text{O}$	$\text{CH}_4$	$\text{Cu}$	$\text{CO}_2$	$\text{H}_2\text{O}$
$\Delta H$ (kJ/mol)	-173.2	-74.81	0	-393.51	-285.83
$\Delta G$ (kJ/mol)	-150.6	-50.82	0	-394.38	-273.25
$\Delta S$ (J/(mol*K))	92.9	186.31	33.1	213.67	70.08

$$\Delta H = -197,56 \text{ kJ/mol}; \quad \Delta G = -215,66 \text{ kJ/mol} \quad \Delta S = 60,72 \text{ J/(mol*K)}$$

The reduction of copper oxide with methane occurs under standard conditions. It is sufficient to give the initial activation energy for the onset of the reaction. This is because the reduction reaction of copper oxide with methane is exothermic, meaning that heat is released as a result of the reaction, and this heat acts as an activation energy for the next colliding molecule.

**Table 4.** Appropriate thermodynamic quantities of substances (298 K)

Substance	Fe <sub>2</sub> O <sub>3</sub>	CH <sub>4</sub>	Fe	CO <sub>2</sub>	H <sub>2</sub> O
$\Delta H$ (kJ/mol)	-822	-74.81	0	-393.51	-285.83
$\Delta G$ (kJ/mol)	-740	-50.82	0	-394.38	-273.25
$\Delta S$ (J/(mol*K))	87	186.31	27.15	213.67	70.08

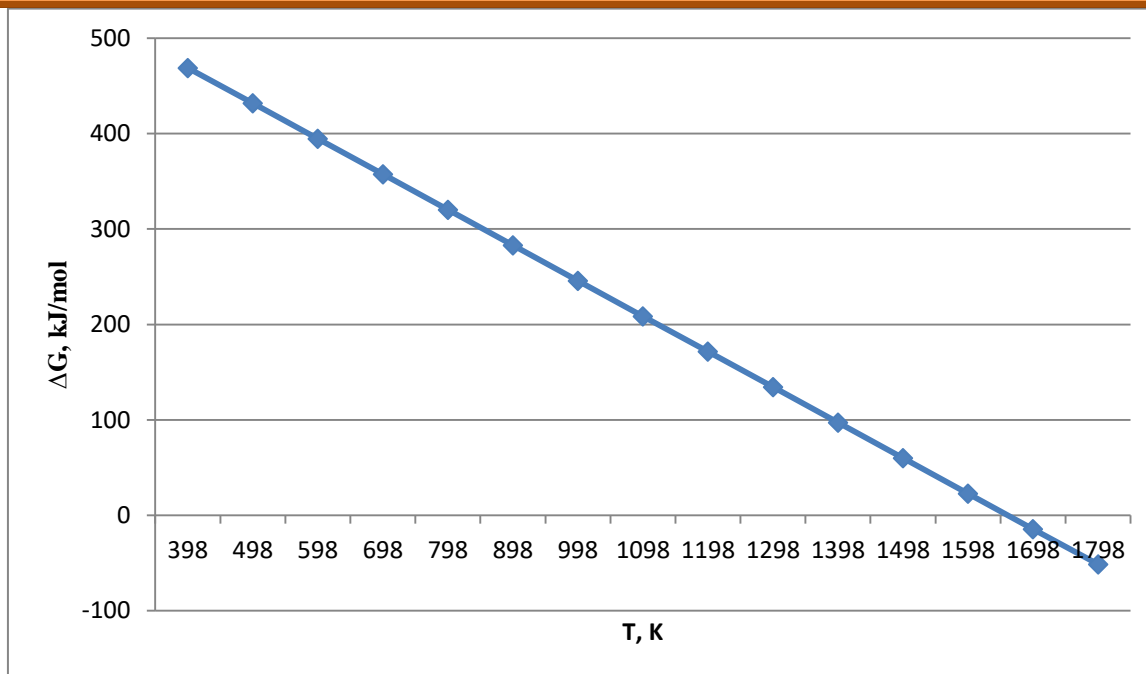
$$\Delta H = 616,92 \text{ kJ/mol}; \quad \Delta G = 505,82 \text{ kJ/mol}; \quad \Delta S = 371,76 \text{ J/(mol*K)}$$

The values calculated under the standard conditions above show that the reduction reaction of high iron oxide with methane gas does not occur spontaneously at 298 K. The enthalpy of the reaction also showed the heat absorption. Therefore, it is necessary to determine the temperature required for the optimal flow of this reaction. To do this, we first need to construct the equation of dependence of the Gibbs energy of the reaction. The free energy equation for the reduction reaction of high iron oxide with methane is as follows:

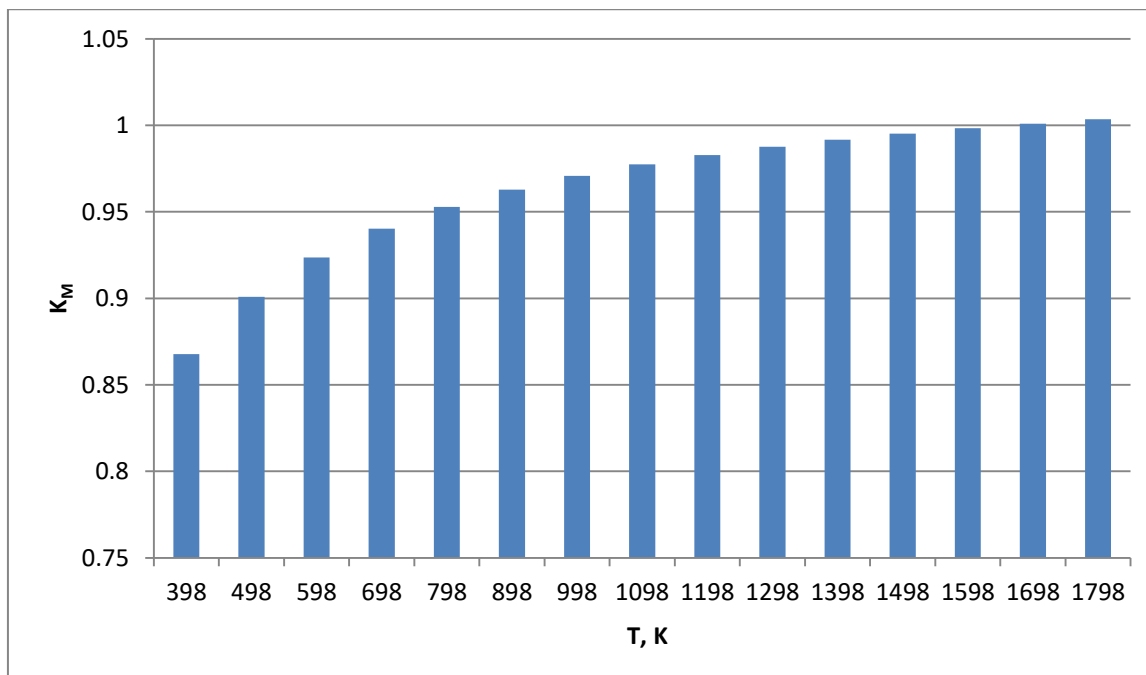
$$\Delta G = 616,92 - 0,37176 * T$$

**Table 5.** Values of the free energy of the reduction reaction of high iron oxide with methane at different temperatures

No	T	G	LnK <sub>M</sub>	K <sub>M</sub>
1	398	468,96	-0,142	0,8678
2	498	431,78	-0,104	0,9009
3	598	394,61	-0,079	0,9237
4	698	357,43	-0,062	0,9402
5	798	320,26	-0,048	0,9529
6	898	283,08	-0,038	0,9628
7	998	245,9	-0,03	0,9708
8	1098	208,73	-0,023	0,9774
9	1198	171,55	-0,017	0,9829
10	1298	134,38	-0,012	0,9876
11	1398	97,2	-0,008	0,9917
12	1498	60,024	-0,005	0,9952
13	1598	22,848	-0,002	0,9983
14	1698	-14,33	0,001	1,001
15	1798	-51,5	0,0034	1,0035



**Figure 2.** Temperature dependence of the free energy of the reduction reaction of high iron oxide with methane



**Figure 3.** The temperature dependence of the equilibrium constant of the reduction reaction of high iron oxide with methane

The results of thermodynamic analysis of the oxidation of metal sulfides showed that the oxidation of chalcopyrite in the initially abundant oxygen atmosphere results in the formation of ferrites consisting of copper and iron oxides. This negatively affects the next stage, the separation of iron and copper. Because copper ferrite has weak magnetizing properties. Therefore, the study carried out a selective recovery process involving methane gas in a weakly regenerating atmosphere. The slowest step is the reduction of iron (III) oxide, which begins at 1386 °C. Copper oxide already has an optimal recovery rate at 350 °C. This means that in the process of reduction with methane, selective reduction of copper oxide is achieved when the temperature range is 350-400 °C. As a result of recovery, the remaining product contains a mixture of metallic copper powder and iron oxides that have not yet recovered. From this

product, iron oxides can be separated by magnetic separation and sent as a primary raw material for iron production. The resulting metallic copper powder is supplied to the consumer as a finished product.

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