THERMODYNAMIC AND KINETIC CONSIDERATIONS OF THE CARBOTHERMIC REDUCTION OF ORES BASED ON IRON AND COPPER OXIDES

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Abstract: *The chemical reduction of iron ores has played a significant role in human history for thousands of years, dating back to the Iron Age. This presentation focuses on carbothermic reduction in the solid state and explores the potential to use iron oxides as a secondary source of iron and energy. Various mechanisms for the interaction of solid reactants at temperatures below 1000°C are discussed. An emphasis is given to the potential of carbothermal dissociation of iron and copper oxides based on a process mechanism involving dissociative evaporation and simultaneous condensation of the product. The presentation also includes kinetics modeling, calculations of main kinetic parameters, and theoretical thermodynamic calculations. It concludes with a discussion on the potential of extracting other valuable metals from oxides by using the carbothermic reaction in the solid state.*

Key words: REACTION MECHANISM, CARBOTHERMIC REDUCTION, DISSOCIATIVE EVAPORATION, IRON OXIDE, COPPER OXIDE

INTRODUCTION

Chemical reduction of the iron ores has been an essential part of human history for the last 4000 to 5000 years, dating back to the beginning of the Iron Age [1,2]. Today, carbothermic reduction in solid state is gaining increased attention due to the potential to utilize iron oxides as a secondary source of iron [3,4] or energy [5], or due to the reducing consequences of the formation of greenhouse gases and environmental contamination associated with the conventional processes [6,7]. Various mechanisms have been suggested to explain how the solid reactants (oxide and carbon) interact at temperatures below 1000 °C to produce solid metal. The most common mechanism involves the reduction of oxides through gaseous intermediates CO and CO_2, as shown in the following reactions:

$$MO(s) + CO \rightarrow M(s) + CO_2 \quad (1)$$

$$CO_2 + C(s) \rightarrow 2CO \quad (2)$$

Baikov [8] and later Ryabchikov et al. [9] attempted to utilize a thermal dissociation scheme to interpret the carbothermal reduction mechanism by direct reduction reactions, as given in equations (3) and (4).

$$MO(s) \rightarrow M(s) + 1/2O_2 \quad (3)$$

$$C(s) + O_2 \rightarrow CO_2 \quad (4)$$

However, the opinion is that the equilibrium partial pressure of oxygen for reaction in equation (3) is too small to explain the achieved reduction rates. At 1000 ^oC, the partial pressure of oxygen is 2×10^{-17} atm for FeO and 1×10^{-8} atm for Cu_2O. Because of this, most researchers usually reject this explanation regarding iron and copper oxides.

Another approach proposed in the late 1980s, considers the oxide reduction involving the formation of gaseous carbides through the interaction of metal vapor with carbon [10,11].

$$2MO(s) + MC_2(g) \rightarrow 3M(g) + 2CO \quad (5)$$

$$2C(s) + M(g) \rightarrow MC_2(g) \quad (6)$$

Mass spectrometry's direct observation analyses revealed the existence of metals in elemental form and corresponding gaseous carbide vapors. It is further used to interpret the kinetics of carbon's interaction with the oxides of different elements. However, contrary to preliminary expectations, this mechanism cannot be applied to reducing the majority of oxides of interest due to the low saturated pressure of metals at reduction temperatures and the impossibility of transporting metal vapor to carbon in line with the reaction described by equation (6).

This presentation aims to assess preliminary experimental results and discuss the potential of the carbothermal dissociation of iron and copper oxides by process mechanism based on the dissociative evaporation of the reactant with simultaneous condensation of the low-volatile product.

KINETICS MODELING

The calculations are based on the classical evaporation model of Hertz-Langmuir, which has been expanded to include cases of dissociative evaporation of compounds. The theoretical calculation of the main kinetic parameters, such as the flux of the gaseous product (J), the rate constant (k), the product partial pressure (P), and the parameters of the Arrhenius equation (E_a and A), has been acquired from the thermodynamic databases. In the case of a binary compound A_xB_y decomposing in a vacuum into gaseous products, equation can be written as follows:

$$zA_xB_y(s) \rightarrow aA(g) + bB(g) \quad (7)$$

the flux of product A can be expressed through the equivalent partial pressure P_A of this product corresponding to the hypothetical equilibrium of reaction (7) in the following form:

$$J_A = \frac{\gamma M P_A}{\sqrt{(2\pi M_A RT)}} \quad \text{..... (8)}$$

where M and M_A are the molar masses of the reactant and product A, γ is the unit conversion coefficient (e.g., from atmospheres to Pascals), and R is the gas constant.

The partial pressure of product A (P^e_A) can be calculated using the equilibrium constant K_p for reaction (7). When there is no excess of reaction products in the reactor atmosphere, which corresponds to the equimolar evaporation mode (τ=0.5), the partial pressure P_A can be expressed as per reference [12]with following equation:

$$P^e_A = a\left(\frac{K_p}{F}\right)^{1/v}\left(\frac{M_A}{M_B}\right)^{b/2v} = \frac{a}{F^{1/v}}\left(\frac{M_A}{M_B}\right)^{b/2v}\exp\left(\frac{\Delta_r S^0_T}{vR}\right)\exp\left(-\frac{\Delta_r H^0_T}{vRT}\right) \quad \text{..... (9)}$$

Where:

$$F \equiv a^a * b^b \quad \text{..... (10)}$$

$$v = a + b \quad \text{..... (11)}$$

and

$$K_p = P^a_A * P^b_B \quad \text{..... (12)}$$

Following the process described by equation (7), $\Delta_r H^0_T$ and $\Delta_r S^0_T$ represent the changes in enthalpy and entropy, respectively. If the partial pressure P'_B of one of the gaseous components is much higher than the equivalent pressure P_B of the same component released in the decomposition, and if P'_B remains constant during the decomposition process, we refer to this evaporation mode as isobaric.

$$P^i_A = \frac{K_P^{1/a}}{(P'_B)^{b/a}} = \frac{1}{(P'_B)^{b/a}}\exp\left(\frac{\Delta_r S^0_T}{aR}\right)\exp\left(-\frac{\Delta_r H^0_T}{aRT}\right) \quad \text{..... (13)}$$

As seen in equations (9) and (13), the calculated activation energies for reaction (7) should differ between the equimolar and isobaric modes of decomposition. Therefore, the activation energy for the equimolar mode is:

$$E^e_a = \frac{\Delta_r H^0_T}{\gamma} \quad \text{..... (14)}$$

while the isobaric mode is:

$$E^i_a = \frac{\Delta_r H^0_T}{a} \quad \text{..... (15)}$$

Table 1 presents the values of the thermodynamic functions for the discussed reactions without considering condensation energy transfer. The most likely mechanism of energy transfer seems to be thermal accommodation [13], which involves the direct transfer of energy at the reaction interface through collisions between low-volatile molecules and

the surfaces of the reactants and products. When the solid phases are at equal temperatures, we can anticipate an equal energy distribution between the two phases, i.e., τ=0.5.

Table 1, Investigated chemical reactions and corresponding thermodynamical parameters [14,15,16]

	$\Delta_r H^0_T$ (kJ/mol)				$\Delta_r S^0_T$ (J/molK)		
Reaction	1000 K	1300 K	1600 K		1000 K	1300 K	1600 K
Fe(s)=Fe(g)	409.5	402.1	398.0		143.4	136.7	131.0
$FeO(s)=Fe(g)+1/2O_2$	675.7	669.4	662.6		205.2	199.7	195.0
$FeO(s)=Fe(s)+1/2O_2$	266.1	267.4	264.6		61.8	63.0	64.1
Cu(s)=Cu(g)	332.8	330.8	-		126.2	124.0	-
$Cu_2O(s)=2Cu(g)+1/2O_2$	838.8	830.5	-		319.2	313.5	-
$Cu_2O(s)=2Cu(s)+1/2O_2$	172.8	168.8	-		66.0	65.5	-

RESULTS AND DISCUSSION

The characteristic periods of the carbothermic reduction processes are induction, autocatalytic acceleration, and relaxation. The most important parameters of carbothermic reduction processes are initial temperatures and values of the activation energies.

The autocatalytic characterization of the carbothermic reduction means that once the reaction is initiated, the rate of isothermal reduction accelerates as the reduction progresses, reaching a maximum. Representative examples of the variation in the reduction rate with the degree of reduction in a vacuum for Fe and Cu oxides are shown in Figure 1.

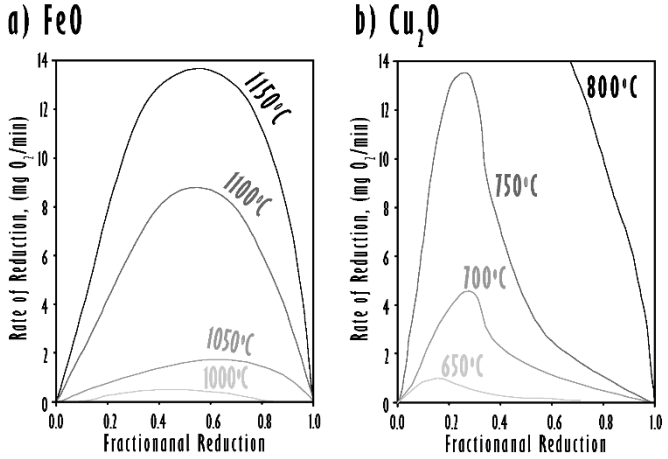

Figure 1, Typical carbothermic reduction curves, a) reduction of FeO by carbon in vacuum at different temperatures[17], *and b) reduction of Cu_2O by carbon in vacuum at different temperatures*[18]

The interpretation of the origin of these induction and acceleration periods involves the process of congruent dissociative evaporation, along with simultaneous condensation of the low-volatility product at the reactant/product interface. This approach involves transferring condensation energy to the reactant (oxide), increasing its decomposition rate. During the initial decomposition stage, when there are no nuclei on the reactant surface to facilitate condensation of the low-volatile product vapor at the interface zone and energy transfer to the reactant, the decomposition proceeds much more slowly. The time it takes to form the first nuclei on the surface of the reactant is known as the induction period. This approach also allows for the mechanism of nucleation through condensation of supersaturated vapor of the low-volatility product (metal) to be described explicitly [13].

The presence of defects or foreign impurities on the surface can be compared to the appearance of nuclei in a new phase. This results in shorter or completely disappearing induction and acceleratory periods - the time during which the product film covers the entire surface of the reactant and the reaction reaches a steady state [19].

As a criterion for theoretically estimating the initial reduction temperatures, two critical parameters are used: the average initial radius of oxide particles, r_0, and the total decomposition time, t_0. Upon integration of the equation:

$$J = -\left(\frac{dm}{dt}\right)\left(4\pi r^2\right)^{-1} \quad \text{..... (16)}$$

and further considering Eq. (8) by applying the relationship between sphere volume and metal density, $m = (4/3)\,\pi\, r^3\rho$, where m, r, and ρ represent the mass, radius, and density of the reactant spherical particle(s), respectively, a simple expression is derived:

$$P_B = \left[\frac{\rho(2\pi M_B RT)^{1/2}}{\gamma^M}\right]\left(\frac{r_0}{t_0}\right) \quad \text{..... (17)}$$

Although experimental values were obtained under various conditions, and the initial temperatures for the thermal decomposition of oxides at a certain pressure and temperature were calculated using specific equations and thermodynamic functions, a comparison of the calculated and experimental values shows that the temperature differences for various metals do not exceed 100 °C.

Figure 2 shows the Arrhenius plots for the carbothermic reduction of Fe and Cu oxides. These plots are based on experimental data from various sources presented in graphical or tabular form. A standard linear regression correlation is used to calculate the activation energies and standard deviations. Table 2 lists the data and the theoretical results calculated from equations (14) and (15).

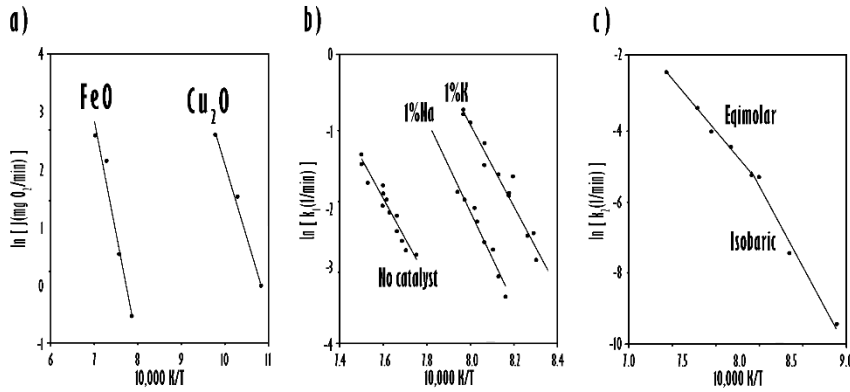

Figure 2, Arrhenius plots for the carbothermic reduction, a) FeO and Cu_2O constructed from [20,21]*, b) FeO constructed from* [22]*, and c) FeO constructed from* [23]

In Figure 2, various parameters were plotted on the ordinate axes. Figure 2a shows the mass of oxygen loss (J) per 1 g of oxide in 1 minute. Figures 2b and 2c display the k_1 coefficient in the Prout-Tompkins equation [24] and the rate constant k_2 for first-order kinetics, respectively. Despite their differences, these plots can be compared based on their position along a temperature scale.

The Arrhenius plots for the reduction of FeO shown in Figure 2 reveal two sets of activation energies, distinguished by an average factor of 1.5. This aligns well with the expectation of two modes (isobaric and equimolar) for the dissociative evaporation scheme. The same concept is typically applied to interpret similar patterns observed in other decomposition reactions, such as the dehydration of some hydrated salts.

The isobaric mode of FeO decomposition has been observed only under conditions of argon flow when the partial pressure of residual oxygen in argon exceeds the equivalent pressure of oxygen (1×10^{-7} atm) at the initial temperature. Such a situation is unlikely in a high vacuum. The difference in the decomposition modes observed at high temperatures (above 1000 ºC) in [22], and [23] is probably due to the different content of oxygen in argon. This is supported by a remark in [23] that purified argon gas was used in this work. For that reason, in Figure 2c, two regions are observed in the Arrhenius plot: isobaric and equimolar, respectively, at lower and higher temperatures.

The plots in Figure 2b show a significant impact of Na_2CO_3 and K_2CO_3 additions on the rate of carbothermal reduction. This is due to the decrease in the partial pressure of oxygen in the argon flow caused by the activation of the reducing properties of graphite in the presence of alkali metals. This activation is likely the result of the formation and subsequent decomposition of compounds made up of Na and K with carbon at a high temperature, leading to structural deformation of graphite particles [25]. The experiments described in [26] confirmed the activation effect of alkalis on graphite. The plot shift in the presence of 1% K_2CO_3 to a lower temperature (Figure 2b) corresponds to a 28-fold increase in the rate constant or around a three-orders-of-magnitude decrease in the partial pressure of oxygen.

Table 2, Activation energies for thermal decomposition of investigated oxides

	E_a, (kJ/mol)	
	Calculated	**Experimental**
FeO	312 (Equimolar model)	331 [17], 305 [23]
	468 (Isobaric model)	465 [22], 463 [23]
Cu_2O	202 (Equimolar model)	205 [18]

FeO AND Cu_2O DECOMPOSITION IN EFFUSION (KNUDSEN) CELLS

An interesting consequence of the proposed mechanism for carbothermic reduction of oxides is the potential for the process to occur even without carbon. Carbon's role in this process is to react with the oxygen released from the decomposition of the oxide, thereby maintaining a low partial pressure of oxygen in the system. Under atmospheric pressure or in the presence of an inert gas, extracting oxygen from this volume is hindered by diffusion limitations. However, under high vacuum conditions, this extraction should be efficient enough. This suggests that the dissociative evaporation of oxide with simultaneous condensation of metal can occur in a high vacuum, even without carbon.

Careful assessment of the investigation on the FeO and Cu_2O dissociation results in an effusion (Knudsen) cell [27] revealed that these oxides dissociate, forming solid metals inside the cell. In addition, research conducted on Ni [28, 29] and Co [30] oxides showed these metals in metallic form on the interior surfaces of the Knudsen cells. More importantly, these results contradict what would be expected from the thermodynamic equilibrium of the simple metal dissociation reaction:

$$MO(s) \rightarrow M(g) + \tfrac{1}{2}\, O_2 \quad \text{..... (18)}$$

The results presented in Table 3 show that the equilibrium partial pressure of Cu for the gaseous dissociation of its oxides is similar to the equilibrium pressures of metal vapor over solid metals. However, for Fe, it is much smaller. At lower temperatures, this difference is even more pronounced. This is by comparing the activation energies for these two processes in Table 3. Therefore, if the dissociation mechanism follows the equilibrium described by equation (18), the formation of metal in the condensed phase (solid or liquid) is unlikely for Cu and would be impossible for Fe.

Table 3, The equilibrium pressures and activation energies associated with the gaseous dissociation of oxides and the evaporation of metals

Oxide	**T (K)**	**P_M (atm)**			**E_a (kJ/mol)**	
		Dissociation	Evaporation		Dissociation	Evaporation
FeO	1700	$2.1*10^{-7}$	$4.1*10^{-6}$		442	398
Cu_2O	1500	$1.3*10^{-5}$	$8.1*10^{-6}$		329	316
Cu_2O	1300	$2.1*10^{-7}$	$1.5*10^{-7}$		332	331

The metals' appearance in metallic form in Knudsen cells, unforeseen by theoretical considerations, can be explained by the dissociative evaporation of oxides, which leads

to the simultaneous condensation of metal vapor at the oxide/metal interface. During this process, some condensation energy is transferred to the oxide. This mechanism occurs at much lower temperatures than oxides' simple gaseous dissociation without considering energy transfer. Additionally, the partial pressure of oxygen discharged from the Knudsen cell is expected to be higher than the equilibrium pressure over the MO(s)-M(s) system. Experimental data from various publications [31, 32, 33] shows that the experimental partial pressures of oxygen are consistently about an order of magnitude higher than the equilibrium pressures for the condensate dissociation of oxides. Therefore, both of these facts (the presence of metals in the condensed phase and partial pressure of oxygen higher than equilibrium) can be considered additional supporting arguments for the proposed mechanism.

CONCLUSIONS

The analyses conclude that the carbothermic reduction of iron and copper oxides is typical of many other solid-state decomposition reactions. Thermodynamic considerations imply that the reduction mechanism can be described as the dissociative evaporation of oxide with the simultaneous condensation of metal at the oxide/metal interface. The mechanism is quantitatively interpreted by essential features, such as initial temperatures and activation energies. It also explains the induction and acceleration periods in the reduction process. A similar carbothermic reduction process may occur for oxides of other metals, such as those in the platinum group, silver, and gold. The oxides of these elements are unstable, and their volatility at decomposition temperatures below 1000 ^{o}C is very low. However, with the increase in volatility at decomposition temperature, if the metal remains in the gaseous phase at the temperature of oxide reduction, the above-described mechanism would not work. Considering thermodynamic data, this is the case for elements such as Al, Cr, Mg, Mn, Sn, Zn, etc. Their carbothermic reduction most likely occurs through the gaseous carbide mechanism.

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