Thermodynamic and Equilibrium Composition Analysis of Using Iron Oxide as an Oxygen Carrier in Nonflame Combustion Technology

Jiayu Xin,　Hua Wang*,　Fang He,　Zhimin Zhang

Faculty of Materials and Metallurgical Engineering, Kunming University of Science and Technology, Kunming 650093, China

Abstract: Nonflame combustion technology (NFCT) is a harmonious energy utilization technology. There are not environmental-unfriendly gases such as NO_x, CO_2 discharged in the whole combustion process. Combustion processes realizes zero emission through this technology. Fe_2O_3 is involved as oxygen carrier, is examined thermodynamically, and the thermodynamic data of the redox reactions are calculated. Using the criteria of minimizing the Gibbs free energy, the equilibrium composition was investigated. The equilibrium analysis shows that producing complete oxidized resultants must have high molar ratio of Fe_2O_3/CH_4. If quantity of Fe_2O_3 is not sufficient, more partial oxidized products such as CO, H_2, even C will be produced.

Key words: nonflame combustion technology, thermal cyclic carrier, molten salt, equilibrium composition, thermodynamic analysis

1. Introduction

The utilization of fossil fuels causes serious negative impacts on the environment and human life. There are many pollutants such as SO_x, NO_x and CO_2 emission produced from the combustion of coal, oil and natural gas. It has been known for more than 100 years that CO_2 is a greenhouse gas and that the release of CO_2 from fossil fuel combustion may affect the climate of the earth. In the last years the concern over the aspects of an increased release of greenhouse gases has been growing greatly. Reducing carbon dioxide (CO_2) emissions to alleviate global warming has become an international issue in recent years. Some countries committed themselves to legally binding emissions targets and timetables for reducing their greenhouse gas emissions which has

been signed in December 1997 at then meeting in Kyoto, Japan. Under the Kyoto Protocol to the United Nations Framework Convention on Climate Change (UNFCCC), these industrialized countries together must reduce their emissions of six kinds of greenhouse gases by at least 5% below 1990 levels over the commitment period of 2008-2012 [1].

One strategy to decrease CO_2 emissions is to separate the CO_2 from the fuel gas and to store it. There are several suggestions and methods [2–4] for sequestrating CO_2 such as storage it in used oil and gas fields, in deep coal beds, in aquifers, or deep-sea and deep-sea bottom storage. However, the CO_2 capture technologies have advantages and disadvantages when installed in a power-generation system. Initial evaluations performed by Herzog *et al*. [5] indicated that certain technologies for CO_2 control from flue gas formed from conventional power plants would create substan-

tial losses of their thermal efficiency. The technology introduced in this paper is suggested by combining the knowledge of energy chemistry, fuel cell and combustion science & technology. This technology is a novel revolutionary combustion process based on thermal cyclic carriers of molten salt. It is supposed zero emission can be realized during the combustion process through the use of the suggested technology [6].

2. Concept of NFCT

Figure 1 is the conceptual schematic of the NFCT [7]. As shown in Figure 1, the first part of the process is the section of producing oxide, and there are molten salts and oxides in this reactor. Air driven by an air compressor or other equipment goes through the reactor. When air contacts with the molten salts and oxides, O_2 in air is absorbed into the molten salts and oxides through physical and chemical reactions. Theoretically, if the airflow is controlled properly, all of the O_2 in the air can be absorbed into the media. So, as the only outlet gas, pure N_2 can be recycled as commercial products. And then the molten salts

and oxides are pumped into another reactor, namely the section of combustion. In this chamber, fuels are blown into the molten bath, *i.e.* the media of carrying heat and oxide, and the oxygen element absorbed into the media at first stage is released and interacted with fuels when the fuels come across the oxides. In many cases, if the fuels react completely with oxide, only three kinds of products could be formed, *i.e.* water vapor, CO_2 and thermal energy in this stage. CO_2 can be easily separated from water and used as a commercial product or chemical raw material, and heat is stored in the media of heat carrier. In the heat exchanger, heat is transferred from heat carrier to water, air or other media, and made it come into utilization. It is necessary to notice that nitrogen and sulfur elements are absorbed into molten salt instead of being fired in the section of combustion. This can be partly explained by the fact that the fuels react with oxides through chemical reactions rather than react with O_2 directly. From the conceptual scheme, we can see that there are no hazardous gases discharged into air during the whole combustion process. So this combustion system is a clean, zero emission combustion process.
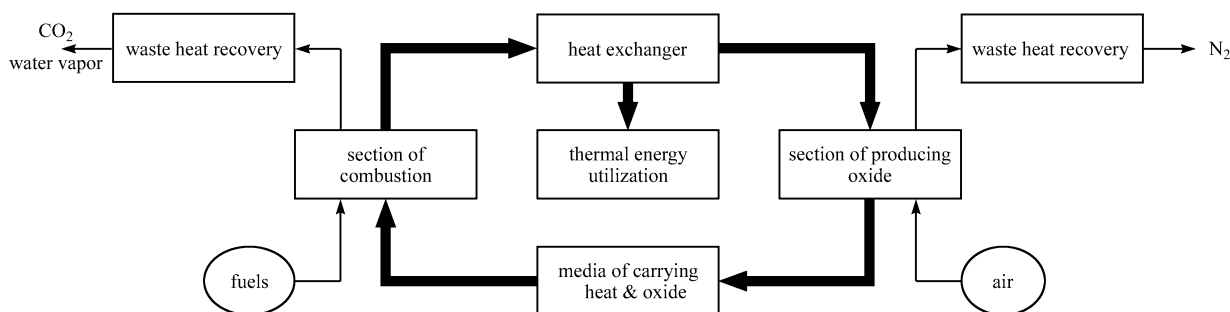

Figure 1. Conceptual schematic of nonflame combustion technology

Generally speaking, NFCT does have several apparent advantages. They can be summarized as follows (a) there are only two kinds of by-products CO_2 and water vapor to be discharged when fuels combust completely in the section of combustion. Thus the greenhouse gas is fundamentally eliminated to emit into air because pure CO_2 can be easily recycled as a chemical raw material. (b) NO_x is prevented to be formed due to the lower temperature in the section of producing oxide and there is not nitrogen element in the section of combustion. (c) Sulfur and heavy metals are absorbed into molten salt instead of being discharged during the combustion because all reactions are carried out in the molten salt. (d) The technology realized zero emission during combustion process.

## 3. Thermodynamic analysis of using iron oxide as an oxygen carrier in nonflame combustion technology

Thermochemical calculations are based on enthalpy H, entropy S, heat capacity C_p and Gibbs energy G values for chemical species. All of them can be mathematically derived from experimental observations. Data for calculations come from thermodynamic data handbook [8] referring reference [9] which are used for detailed thermodynamic calculation.

Usually, the conventional combustion reaction can be expressed in Reaction 1, if we take carbon as fuel and oxygen as oxidant:

$$C + O_2 = CO_2 \qquad (1)$$

The thermodynamic calculations indicate the standard Gibbs free energy change ($\Delta_r G$) and the enthalpy change ($\Delta_r H$) is negative values in a wide temperature range. That is to say the reaction could occur spontaneously to the right and discharge heat. In our present case of NFCT if we use Fe_2O_3 as an oxygen carrier and carbon as fuel, and suppose that carbon is oxidized completely, the chemical reactions of the two sections take place as follows.

In the section of combustion:

$$2Fe_2O_3 + C = 4FeO + CO_2 \qquad (2)$$

In the section of producing oxide:

$$4FeO + O_2 = 2Fe_2O_3 \qquad (3)$$
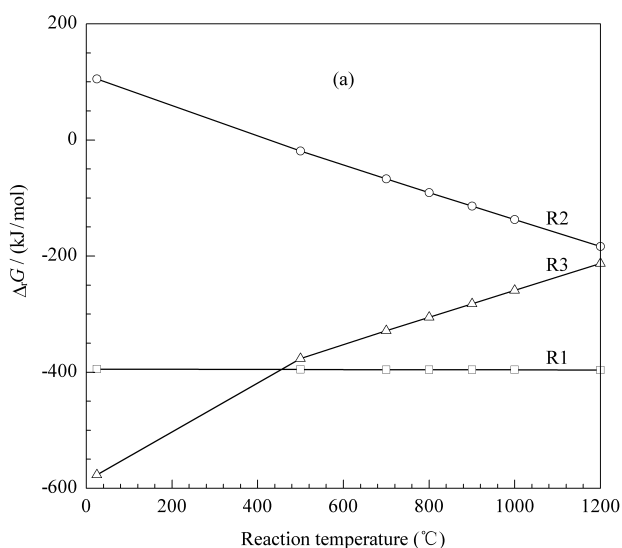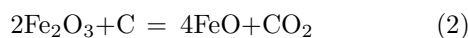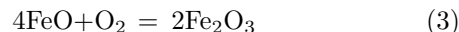
The calculated variations of $\Delta_r G$ and $\Delta_r H$ for these three Reactions 1–3 are shown in Figure 2. In fact, if we add Reaction 2 and Reaction 3, the total reaction would be Reaction 1. Therefore, the thermal energy produced from NFCT should be equal to that produced from the conventional combustion.
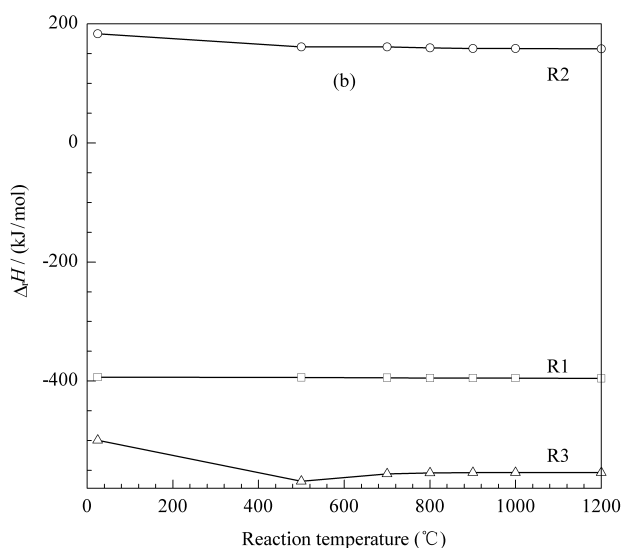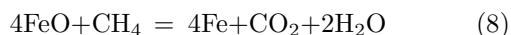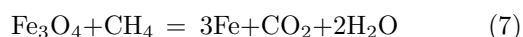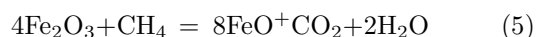

Figure 2. The variations of $\Delta_r G$ (a) and $\Delta_r H$ (b) with temperature for Reactions (1)–(3)

However, if we use carbon as fuel, the reaction carried in the section of combustion is a kind of reaction between solid and solid. The reaction rate of solid-solid reaction is much lower than that of solid-liquid reaction and/or solid-gas reaction [10]. It is difficult to achieve complete combustion in a short time, so we use methane as a fuel to study NFCT. Thus, if the reaction proceeds completely, many reactions may be taken place.
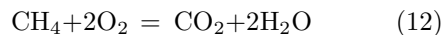
In the section of combustion, the possible reactions are as follows:

$$12Fe_2O_3 + CH_4 = 8Fe_3O_4 + CO_2 + 2H_2O \qquad (4)$$
$$4Fe_2O_3 + CH_4 = 8FeO + CO_2 + 2H_2O \qquad (5)$$
$$4Fe_3O_4 + CH_4 = 12FeO + CO_2 + 2H_2O \qquad (6)$$
$$Fe_3O_4 + CH_4 = 3Fe + CO_2 + 2H_2O \qquad (7)$$
$$4FeO + CH_4 = 4Fe + CO_2 + 2H_2O \qquad (8)$$

In the section of producing oxide, the following three reactions may be carried out:

$$4Fe_3O_4 + O_2 = 6Fe_2O_3 \qquad (9)$$

$$4FeO + O_2 = 2Fe_2O_3 \qquad (10)$$
$$4Fe + 3O_2 = 2Fe_2O_3 \qquad (11)$$
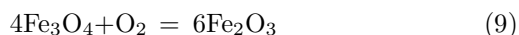
If we add Reaction 4 and Reaction 9 or Reaction 5 and Reaction 10 together, we get:

$$CH_4 + 2O_2 = CO_2 + 2H_2O \qquad (12)$$

This is the conventional combustion of CH_4 with air.

The $\Delta_r G$ and $\Delta_r H$ of Reactions 4–12 are summarized in Figure 3. As indicated in Figure 2–3, we can see that all of reactions take place in the section of combustion are endothermic and the reactions take place in the section of producing oxide are exothermic. This is opposite to conventional combustion. Thermodynamic calculations indicate that these reactions can occur spontaneously in the temperature that we interested. Additionally, thermal energy will be discharged in large quantities during the combustion process.
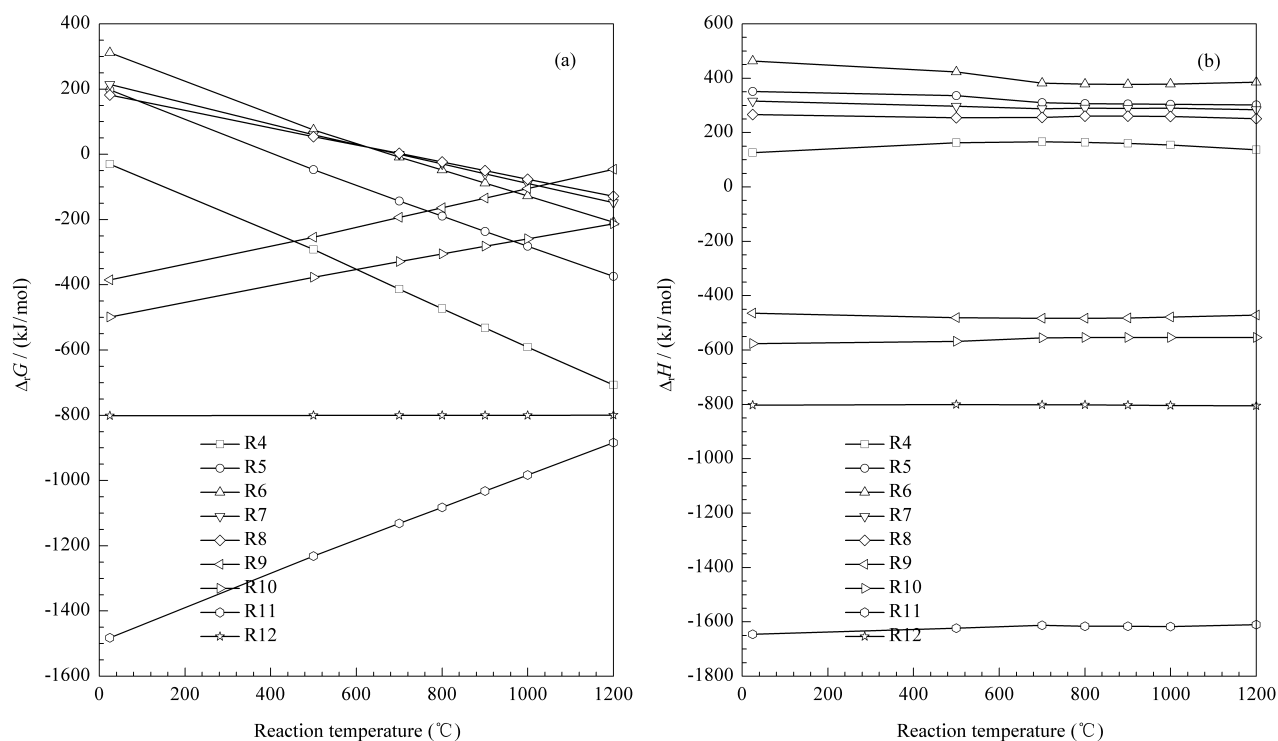
Figure 3. The variations of $\Delta_r G$ (a) and $\Delta_r H$ (b) with temperature for Reactions (4)–(12)

4. Equilibrium composition analysis of CH_4 and Fe_2O_3

However, in practice CH_4 cannot be oxidized to CO_2 and H_2O completely. CH_4 may be partially oxidized to CO or decomposed to C and H_2 at high temperature. Therefore, it is necessary to analysis the equilibrium composition of CH_4 and Fe_2O_3. Using the criteria of minimizing the Gibbs free energy, the equilibrium composition was investigated. HSC Chemistry, which was produced by Outokumpu was used in the calculations.

Figure 4 is the equilibrium compositions at various temperatures when the molar ratio of Fe_2O_3/CH_4 is 4:3, which is the stoichiometric ratio of the reaction between Fe_2O_3 and CH_4 to produce CO_2, H_2O, and metallic Fe. However, from Figure 6 we can see that main components present in the system are H_2 and CO if the temperature is higher than 700 ℃. H_2 concentration has a peak value at about 750 ℃. Carbon deposition is thermodynamically favored at low temperature, but it is constrained at high temperature, and carbon deposition would not exist at the temperature higher than 950 ℃. The conditions of carbon formation are dependent on the amount of oxygen carrier. Carbon deposition is also a problem existing in fuel cell [11] and nature gas reforming [12].
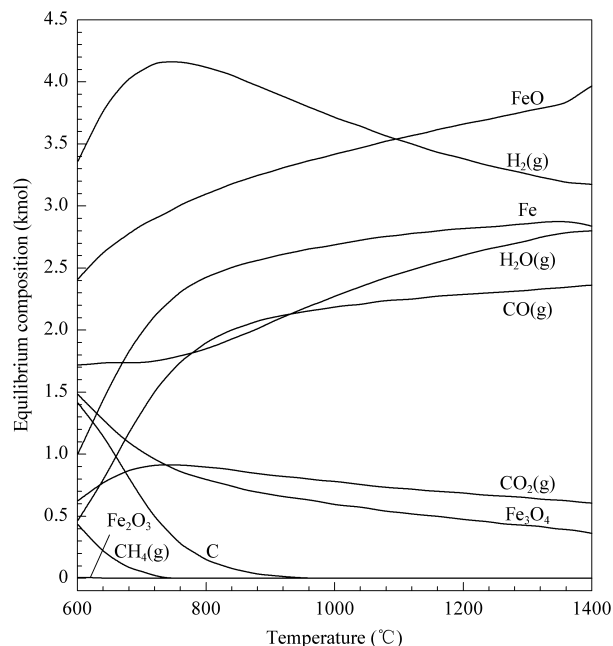

Figure 4. Equilibrium compositions at various temperatures when Fe_2O_3/CH_4 is 4:3

Figure 5 is the equilibrium compositions at various temperatures when Fe_2O_3/CH_4 is 4:1, comparing with Figure 6 with the Fe_2O_3 in excess content, the amounts of fully oxidized products of CH_4, such as CO_2 and H_2O increase as compared to those with

the low Fe_2O_3 and CH_4 ratio. The carbon would be formed due to the excess of CH_4, but not in the present case of the Fe_2O_3/CH_4 molar ratio of 4:1. The peak value of H_2 concentration appears at about 680 °C, which is lower than that in the case of low Fe_2O_3 and CH_4 ratio. The quantity of FeO, H_2O and CO increase and that of CO_2 and Fe_3O_4 decrease with the temperature.
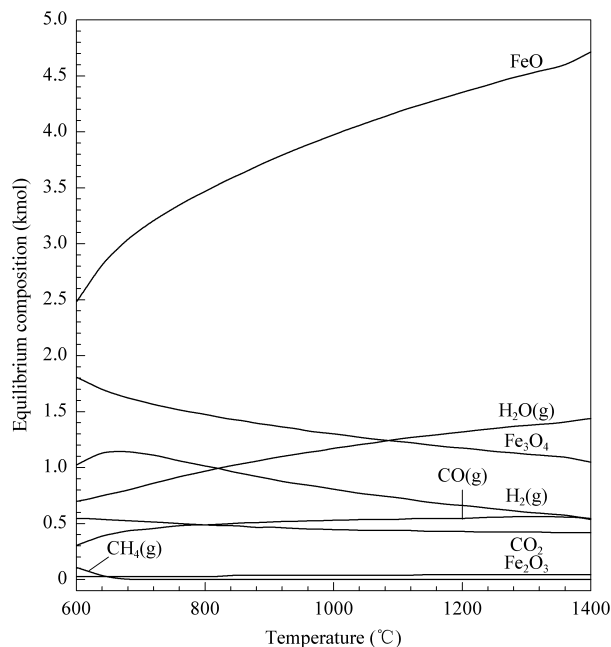

Figure 5. Equilibrium compositions at various temperatures when Fe_2O_3/CH_4 is 4:1

There is no H_2 and CO exists in the condition at high ratio of Fe_2O_3 and CH_4 as shown in Figure 6. Except for some no reactive Fe_2O_3, Fe_2O_3 is preferably reduced to other lower forms of iron oxide such
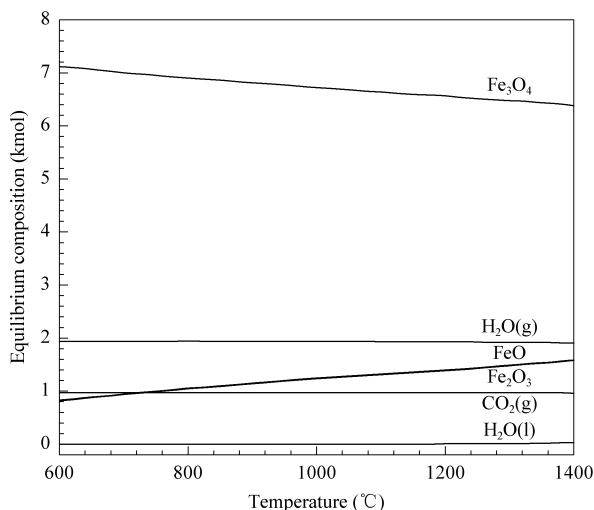

Figure 6. Equilibrium compositions at various temperatures when Fe_2O_3/CH_4 is 12:1

as Fe_3O_4 and FeO, metallic iron could also be formed. The quantity of FeO and Fe_2O_3 increase with temperature, because Fe_3O_4 could decompose and produce Fe_2O_3 and FeO at high temperature.

The ratio of Fe_2O_3/CH_4 may affect the oxidizing ability of the system greatly. Equilibrium compositions at various temperatures when Fe_2O_3/CH_4 is 1:2 are shown in Figure 7. At this ratio, the quantity of Fe_2O_3 is insufficient for complete oxidizing of CH_4. There are too much CO and H_2 with a little CO_2 and H_2O formed in this condition. Fe will be stabilized above 720 °C. The trend of C change is the same as shown in Figure 7, the quantity of C decrease with temperature. All of FeO and Fe_3O_4 could react with CH_4 above 780 °C, and produce metallic Fe.
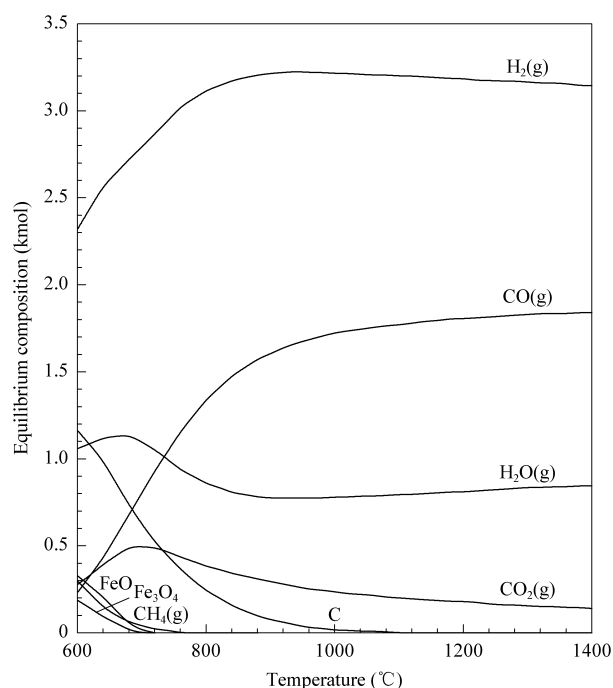

Figure 7. Equilibrium compositions at various temperatures when Fe_2O_3/CH_4 is 1:2

After reacting with fuel, Fe_2O_3 is reduced to Fe_3O_4, FeO even metallic Fe, so the available oxygen element in oxygen carrier decreases, and its oxidizing ability also drops. Oxygen carrier must react with air to regenerate its lattice oxygen. Figure 8 displays the case that Fe reacts with oxygen at a ratio of 4:6. According to this figure, we can see that Fe and oxygen carrier form Fe_2O_3 at a temperature less than 800 °C. However, Fe_3O_4 and FeO appear at a temperature higher than 800 °C. This is due to the decomposition of Fe_2O_3 at high temperature. Reduced ferric oxide such as Fe_3O_4, FeO, Fe can be reoxidized to form lattice oxygen again when oxygen present.
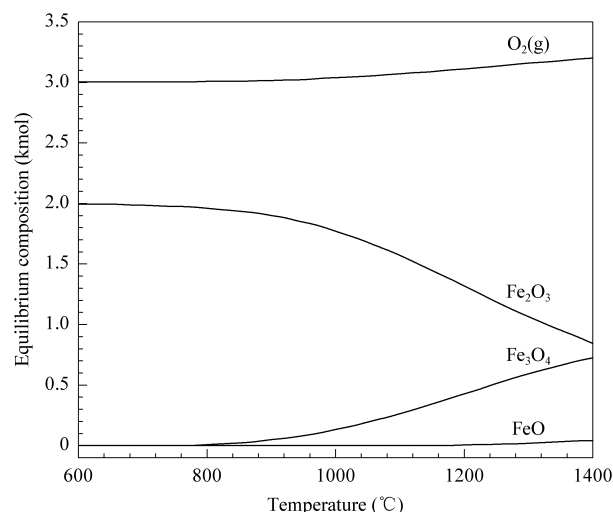
Figure 8. Equilibrium compositions at various temperatures when Fe/O$_2$ is 4:6

Catalytic combustion of CH_4 in molten salt was reported in Reference [13]. It was showed that the highest concentration of CO_2 in outlet gas we obtained was near 85% by using Fe_2O_3 as oxygen carrier. After catalytic combustion of CH_4, air was driven to molten salt to regenerate the lattice oxygen of Fe_2O_3; Fe_2O_3 absorbed nearly all of O_2 in air.

5. Conclusions

Thermodynamic calculations indicate that by using Fe_2O_3 as oxygen carrier nonflame combustion system using thermal cyclic carrier of molten salts is possible. Results show that the systems are thermodynamically favorable over a wide temperature range. Owing to the O_2 and fuels interact respectively with the oxygen media in two different reactors; there are only two types of post-combustion gases, pure N_2 and CO_2, which can be easily recycled. Thus, CO_2 and NO_x are fundamentally eliminated in the whole process. In brief, the NFCT is a type of clean, zero emission and environmental-friendly combustion technology. It has an encouraging potential utilization in the heat and power production industry. The equilibrium analysis shows that in order to produce completely oxidized products, one must use high molar ratio of Fe_2O_3/CH_4. If quantity of Fe_2O_3 is not sufficient, more partial oxidized products such as CO, H_2, even C would be produced.

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