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Thermodynamic Study on Reduction of Iron Oxides by $H_2 + CO + CH_4 + N_2$ Mixture at 900 °C

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Abstract: The reduction gas used in the gas-based direct reduction iron-making process contains CH₄ in different concentrations, which has an important effect on the gas and heat needed for the reduction of iron oxide. To investigate the influence of CH₄ on gas utilization rate and heat needed at 900 °C, the initial conditions are set as H_2 % + CO% = 90, CH₄% + N₂% = 10, gas pressure 1–9 atm, and 0.5 mol Fe₂O₃, and the equilibrium state composition is calculated using the minimum free energy method. The utilization rate of total gas can be improved, and gas demand can be decreased by increasing CH₄ concentration or H₂ concentration or reducing gas pressure. For the production of per ton of Fe from 25 °C to 900 °C, 6.08–7.29 m³ of reduction gas, and 7.338–8.952 MJ of gas sensible heat can be saved by increasing 1 m³ CH₄, while 10.959–11.189 MJ of reaction heat is increased. Compared with 3390.828–3865.760 MJ of the total heat of per ton of Fe for the reduction by H₂ + CO, 2.174–3.703 MJ of total heat is increased by increasing 1 m³ CH₄, and the increase ratio is 0.065–0.096%. This study is helpful to improve the gas efficiency and lower the pursuit of higher concentration of H₂ + CO in reduction gas.

Keywords: thermodynamic model; gas-based direct reduction ironmaking; gas utilization rate; CH₄ conversion; minimized Gibbs free energy principle; equilibrium state; heat needed; reaction enthalpy

1. Introduction

The gas-based direct reduction iron-making process is a kind of non-blast furnace iron-making process which does not use coke and produces solid iron through gas–solid reaction. It is a rapidly developing iron-making process due to its short technological process, high cleanliness, and low CO₂ emission [1]. The basic composition of a gas-based direct reduction iron-making process can be divided into two parts: the gasification process and reduction process [2–6]. The gasification process provides available and clean reduction gas, which requires the concentration ratio of H₂ + CO greater than 85%, the concentration ratio of CO₂ + H₂O less than 5%, the concentration ratio of CH₄ less than 3%, the concentration ratio of H₂S less than 0.1%, and the residual is N₂.

 H_2 and CO are highly efficient in reducing gases. The gas utilization rates of H_2 and CO in the reduction of Fe_2O_3 at 900 °C are 37.575% and 31.460%, respectively, which is the upper limit of the utilization rates of these two gases at 900 °C. Therefore, the reduction utilization rate of the H_2 + CO mixture is between 31.460% and 37.575% [7]. In the presence of CO₂ and H_2O , the reduction



utilization rate of the $H_2 + CO + CO_2 + H_2O$ mixture is further lower. N_2 is often recognized as a heat carrier and does not participate in the reduction reaction in a reduction atmosphere [8]. CO_2 can be removed by pressure swing adsorption or polyamine adsorption, and H_2O can be removed by low temperature or desiccants, while $CH_4 + N_2$ will stay in the reduction gas [9].

The reduction gas generated from CH₄ conversion and coal gasification contain CH₄ in different concentrations, as shown in Table 1 [9–13]. The difference in the concentration of CH₄ between input and output is used to calculate reduction gas demand [11]. In addition, 1 mol CH₄ is often considered to be equivalent to 4 mol H₂ + CO, according to CH₄ conversion Formulas (9) and (10). The chemical reactions in which CH₄ participates in the reduction of Fe₂O₃ are complex and reversible, as shown in Table 2. The main reactions between Fe₂O₃ and H₂ + CO + CH₄ + N₂ include reduction reactions by H₂ or CO or CH₄, CH₄ conversion reactions, carburizing reactions, carbon deposition reaction, water gas shift reaction, gasification reaction, etc. The determination of the equilibrium state containing 11 components requires detailed calculation. It is not reliable to calculate gas demand by only these two chemical equations. Therefore, a specific thermodynamic analysis of the influence of CH₄ on the reduction reaction of Fe₂O₃ is required.

Table 1. The gas composition used for the reduction of iron oxide (volume fraction, %).

Species	CH ₄ Conversion		Coal Gasification					
	HYL III	MIDREX	BG/L	Texaco	Shell	HT-L	Two-Stage	
H ₂ /%	61.8	55–58	27.9	30.78	25.6	30	29.36	
CO/%	23.5	34–37	58.93	39.35	65.1	60	62.38	
H ₂ O/%	0.6	3–4	-	16.43	-	-	1.5	
CO ₂ /%	3.0	1.5-2.5	3.03	11.43	0.8	3.5	2.76	
CH4/%	4.0	0.5–3	6.13	0.04	0.01	<1	0.26	
N2/%	7.1	0.5 - 1	3.35	0.49	8.03	6.2	4.87	
H ₂ S(COS)/%	-	-	-	0.88	0.07	0.02	0.37	

Table 2. The main reactions between Fe_2O_3 and $H_2 + CO + CH_4$ mixture.

Reaction Type	Chemical Reaction Equation					
	$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2 \Delta H^{\ominus}_{298K} = -43.221 \text{ kJ/mol}$	(1)				
CO Reduction reaction	$Fe_3O_4 + CO = 3FeO + CO_2 \Delta H_{298K}^{\Theta OK} = 19.288 \text{ kJ/mol}$	(2)				
CO Reduction reaction	$FeO + CO = Fe + CO_2 \Delta H_{298K}^{\ominus} = -10.920 \text{ kJ/mol}$	(3)				
	$Fe_2O_3 + 3CO = 2Fe + 3CO_2 \Delta H_{298K}^{\Theta} = -23.389 \text{ kJ/mol}$	(4)				
	$3Fe_2O_3 + H_2 = 2Fe_3O_4 + H_2O \Delta H_{298K}^{\ominus} = -2.071 \text{ kJ/mol}$	(5)				
H ₂ Reduction reaction	$Fe_3O_4 + H_2 = 3FeO + H_2O \Delta H_{298K}^{\ominus} = 60.438 \text{ kJ/mol}$	(6)				
112 Reduction reaction	$FeO + H_2 = Fe + H_2O \Delta H_{298K}^{\ominus} = 30.229 \text{ kJ/mol}$	(7)				
	$Fe_2O_3 + 3H_2 = 2Fe + 3H_2O \Delta H_{298K}^{\ominus} = 100.060 \text{ kJ/mol}$	(8)				
CH, conversion reaction	$CH_4 + H_2O = 3H_2 + CO \Delta H_{298K}^{\ominus} = 206.083 \text{ kJ/mol}$	(9)				
CI14 conversion reaction	$CH_4 + CO_2 = 2H_2 + 2CO \Delta H_{298K}^{\Theta} = 247.233 \text{ kJ/mol}$	(10)				
CH ₄ cracking reaction	$CH_4 = C + 2H_2 \Delta H_{298K}^{\ominus} = 74.810 \text{ kJ/mol}$	(11)				
CH reduction reaction	$CH_4 + FeO = Fe + 2H_2 + CO \Delta H_{298K}^{\ominus} = 236.312 \text{ kJ/mol}$	(12)				
CH ₄ reduction reaction	$Fe_2O_3 + 3CH_4 = 2Fe + 6H_2 + 3CO\Delta H_{298K}^{20} = 718.309 \text{ kJ/mol}$	(13)				
	$3Fe + 2CO + = Fe_3C + CO_2 \Delta H^{\ominus}_{298K} = -149.829 \text{ kJ/mol}$	(14)				
	$3Fe + CO + H_2 = Fe_3C + H_2O \Delta H_{298K}^{\Theta} = -108.679 \text{ kJ/mol}$	(15)				
Carburizing reaction	$3Fe + CH_4 = Fe_3C + 2H_2 \Delta H_{298K}^{\ominus} = 97.404 \text{ kJ/mol}$	(16)				
	$3\text{FeO} + 5\text{CO} = \text{Fe}_3\text{C} + 4\text{CO}_2 \Delta H_{298\text{K}}^{\ominus} = -182.590 \text{ kJ/mol}$	(17)				
	$3Fe + C = Fe_3C \Delta H_{298K}^{\ominus} = 22.594 \text{ kJ/mol}$	(18)				
Carbon deposition reaction	$2CO = C + CO_2 \Delta H_{298K}^{\Theta} = -172.423 \text{ kJ/mol}$	(19)				
Water-gas shift reaction	$CO + H_2O = H_2 + CO_2 \ \Delta H_{298K}^{\ominus} = -41.150 \ kJ/mol$	(20)				
Gasification reaction	$C + H_2O = H_2 + CO \Delta H_{298K}^{\Theta} = 131.273 \text{ kJ/mol}$	(21)				

The aim of this study is to investigate the effects of CH_4 concentration, gas pressure, H_2 or CO concentration on reduction gas needed, and reaction enthalpy at 900 °C with CH_4 concentration

less than 10%. This study is helpful to understand the relationship between $H_2 + CO$ and CH_4 in the process of reducing Fe₂O₃ and even to improve the utilization rate of reducing gas by increasing the concentration of CH_4 .

2. Methods

2.1. Parameters Settings

90

0

The initial state and the equilibrium state are shown in Figure 1. The reaction system is composed of solid and gas. The initial solid is 0.5 mol Fe₂O₃, and other gangue in the iron ore are not considered in the reaction system. The initial gas volume fraction is as shown in Table 3. The volume fraction of H₂ + CO is fixed at 90%; namely, CO% + H₂% = 90, which is a common gas composition requirement. For comparison, CO₂ gas and H₂O gas in initial states are neglected in the mixed gas. The volume fraction of CH₄ gas increase from 0% to 10%, and the N₂ is residual.



Figure 1. The initial and equilibrium state of the reaction system.

H ₂ /%	CO/%	CH ₄ /%	N ₂ /%	Σ/%
0	90			
15	75			
30	60			
45	45	0–10, increment 1	Residual	100
60	30			
75	15			

Table 3. The given volume fraction of each component of initial gas.

The reaction temperature is 900 °C, which is used in the MIDREX process and HYL/Energiron process [9,13]. The total gas pressure p_{total} increases from 1 atm 9 atm, and 1 atm (atmosphere) or 1 p^{\ominus} is 101,325 Pa. The total pressure of the reaction system is set to remain unchanged before and after reactions. In fact, the gas pressure decreases from bottom to top of the shaft furnace due to the solid bulk layer.

The amount of the initial gas is 10 mol, which exceeds the amount of gas required for reduction. For the reduction of 0.5 mol Fe₂O₃, the demand for reduction gas, composed of different concentrations of H₂ + CO, are 4.0–4.7 mol, which has been calculated by the minimum Gibbs free energy method [7]. For the H₂ + CO + CH₄ + N₂ gas mixture, the gas demand needs to be calculated under different conditions by the minimum Gibbs free energy method.

2.2. The Minimum Gibbs Free Energy Method

The minimum Gibbs free energy method can be used to calculate the amount of the components in the equilibrium state [7,14,15], which can be obtained from the initial state conditions (amount, temperature, and pressure). Based on the principle of minimum free energy; that is, the sum of Gibbs free energy of each component in the equilibrium state is the smallest, and a calculation model is established, as shown in Formulas (22) and (23). By solving the non-linear equations with constraints, the amount of each component in the equilibrium state could be received.

min.
$$G_{\text{all}} = \sum_{i=1}^{N} n_i G_i = \sum_{i=1}^{N} n_i (G_i^{\ominus} + RT \ln a_i)$$
 (22)

s.t.
$$\sum_{i=1}^{N} \alpha_{ie} n_i = n_e \quad (e = 1, 2, \cdots, M)$$
 (23)

In this two formulas, *i*, *e*, represent the components and elements in the equilibrium state, respectively; *N*, *M*, represent the number of components and the number of elements in the equilibrium state, respectively; n_i , n_e , are the amounts of the components *i* and elements *e* in the equilibrium state, respectively, mol; G_i , G_i^{\ominus} , represent the Gibbs free energy and the standard Gibbs free energy of the components *i*, respectively, J/mol; p_i , p_{total} , p^{\ominus} , represent the partial pressure of the components *i*, the total pressure of all gas, and the standard atmospheric pressure, respectively, Pa, and $p^{\ominus} = 1$ atm = 101,325 Pa; α_{ie} represents the number of element *e* in the component *i*; *T*, represents the thermodynamic temperature of the system, K; R, is the ideal gas constant, which is equal to 8.314, J/(mol·K); a_i represents the activity, when *i* is a gaseous state $a_i = \frac{p_i}{p^{\ominus}} = \frac{n_i}{\sum n_i} \cdot \frac{p_{\text{total}}}{p^{\ominus}}$, when *i* is a solid-state $a_i = 1$. The software LINGO is used in the mathematics calculation of minimum values for nonlinear equations.

2.3. Reaction Enthalpy and Sensible Heat

For reaction enthalpy of chemical reactions and sensible heat of substance with temperature changing, these calculation formulas are the same, which are the difference between the final state and the initial state, as shown in Formula (24).

$$\Delta H = \sum_{i=1}^{N} n_i H_{i, T_i}^{\ominus} - \sum_{j=1}^{M} n_j H_{j, T_j}$$
(24)

where ΔH represents the enthalpy change, kJ/mol, and a negative value is exothermic, a positive value is endothermic; *i*, *j*, signify the components after and before the state change, respectively; *N* and *M* represent the number of components after and before the state change, respectively; *n_i* and *n_j* represent the number of components after and before the state change, respectively, mol; *T_i* and *T_j* represent the thermodynamic temperature of components after and before the state change, respectively, K; H_{i, T_i}^{\ominus} and H_{j, T_j}^{\ominus} , represent the standard molar enthalpy of component *i* at the thermodynamic temperature *T_i* and the component *j* at the thermodynamic temperature *T_j*, respectively, kJ/mol. The standard molar enthalpy and standard molar Gibbs energy of pure matter are derived from the specific heat capacity data provided by previous literatures [16].

2.4. Related Definitions

All equilibrium compositions are calculated by the minimum Gibbs free energy method based on the initial conditions. According to the amount of each component in the initial and equilibrium state, some definitions are made out to search the thermodynamic law in the reduction of iron oxide by reduction gas within CH_4 at 900 °C.

 $CO_2/(CO + CO_2)$ and $H_2O/(H_2O + H_2)$ are used to show the equilibrium gas ratio and the utilization rate of CO and H_2 in the reduction of iron oxide, which is shown in Formulas (25) and (26), respectively.

equilibrium gas ratio of CO₂ =
$$\frac{n_{\rm CO_2, equilibrium}}{n_{\rm CO, equilibrium} + n_{\rm CO_2, equilibrium}}$$
 (25)

equilibrium gas ratio of H₂O =
$$\frac{n_{H_2O,equilibrium}}{n_{H_2,equilibrium} + n_{H_2O,equilibrium}}$$
 (26)

where in the *n* expresses the amount of the component, and the subscript *equilibrium* and *initial* express the equilibrium state and the initial state, respectively.

However, when CH₄ is in the reduction gas, Formulas (25) and (26) are meaningless. According to the mass balance of gas–solid reactions, the lost oxygen in iron oxide is the same as the increased oxygen in gas. The deoxygenation rate of Fe₂O₃ and the utilization rate of total gas are defined as Formulas (27) and (28), respectively. Furthermore, the gas demand can be got by Formula (29). The amount of O in iron oxide is 1.5 mol for 0.5 mol Fe₂O₃, and 600 m³ for Fe₂O₃ including 1 t Fe. CH₄ can save the volume of reduction gas and increase the reaction enthalpy, compared with the reduction gas H₂ + CO, the saving volume of total gas per mol CH₄ and increased reaction enthalpy per mol are defined in Formulas (30) and (31), respectively.

deoxygenation rate of
$$Fe_2O_3 = \frac{\text{the amount of lost oxygen in }Fe_2O_3}{\text{the amount of oxygen in }Fe_2O_3} \times 100\%$$
 (27)

utilization rate of total gas =
$$\frac{\text{the amount of lost oxygen in Fe}_2O_3}{\text{the amount of the initial gas}} \times 100\%$$
 (28)

the amount of gas needed
$$=\frac{\text{the amount of O in iron oxide}}{\text{the utilization rate of total gas}}$$
 (29)

saving volume of total gas per mol
$$CH_4 = \frac{\text{the amount of saving volume}}{\text{the amount of } CH_4}$$
 (30)

increased reaction enthalpy per mol CH₄ =
$$\frac{\left(\Delta H_{\rm CO+H_2+CH_4}^{\ominus} - \Delta H_{\rm CO+H_2}^{\ominus}\right)_{T,P}}{\text{the amount of CH}_4}$$
(31)

 CH_4 conversion is defined as shown in Formula (32). According to the element balance, the possible product from CH_4 are C, Fe₃C, H₂, CO, CO₂, and H₂O. Other hydrocarbons, carbon hydroxide, and carbonates are not considered. CH_4 conversion reflects the utilization rate of CH_4 under specific conditions.

CH₄ conversion rate =
$$\left(1 - \frac{n_{\text{CH}_4,\text{equilibrium}}}{n_{\text{CH}_4,\text{initial}}}\right) \times 100\%$$
 (32)

3. Results and Discussion

3.1. The Equilibrium Composition

The collection of settings are taken as an example to display the law of reduction of Fe₂O₃ by $H_2 + CO + CH_4 + N_2$ mixtures: the initial gas concentration is $H_2\% = 45$, CO% = 45, $CH_4\% = 3.0$, $N_2\% = 7$, the total pressure is 4 atm, and the reaction temperature is 900 °C. Figure 2 shows some rules, such as equilibrium products, equilibrium gas ratio, deoxygenation rate of iron oxide, gas utilization rate, and CH₄ conversion.



Figure 2. The initial gas concentration is $H_2\% = 45$, CO% = 45, $CH_4\% = 3$, $N_2\% = 7$, the total pressure is 4 atm, and the temperature is 900°C. (a) the amount of equilibrium products; (b) equilibrium gas ratio; (c) deoxygenation rate of Fe₂O₃ and utilization rate of total gas; (d) CH₄ conversion rate.

Figure 2a shows the amount and kinds of equilibrium products with increasing the amount of initial reduction gas at the current setting, which demonstrates that the composition of equilibrium products is significantly affected by the quantity of reduction gas. With the increase of reduction gas, the iron oxide follows the law of gradual reduction, that is, $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow Fe_{0.95}O \rightarrow Fe$. When the initial amount of reduction gas is 1.5–2.5 mol and the initial iron oxide is 0.5 mol Fe_2O_3 , the equilibrium state is $Fe_{0.95}O \rightarrow Fe$ stage. Also, any two stages cannot exist at the same time in thermodynamics. Under the current initial conditions, Fe_3C and C have not been generated. The complete reduction of

iron oxide is shown in Figure 2a that product $Fe_{0.95}O$ gradually decreases to 0, and the corresponding amount of product Fe gradually increases to a maximum of 1mol and then remains unchanged. There is a certain amount of reduction gas that is just enough for the iron oxide to be completely reduced, and the more amount of reduction gas is not needed. Besides, attention should be paid to the fact that the content of CH₄ in Figure 2a is close to 0.

Figure 2b shows the equilibrium gas ratio with increasing the amount of initial reduction gas in the current setting. In the reduction stage of $Fe_{0.95}O \rightarrow Fe$ stage at 900 °C, the equilibrium concentration ratios of $H_2O/(H_2 + H_2O)$ and $CO_2/(CO + CO_2)$ are 37.581% and 31.450%, respectively, which are the same as that of the reduction of iron oxide by pure H_2 and pure CO. The two equilibrium concentration ratios are a function of temperature, regardless of whether CH_4 exists or not, or how much CH_4 exists.

Figure 2c shows the deoxygenation rate of Fe₂O₃ and the utilization rate of total gas with increasing the amount of initial reduction gas at the current setting. In the presence of CH₄, the equilibrium concentrations of H₂O/(H₂ + H₂O) and CO₂/(CO + CO₂) cannot represent the utilization rate of the gas. The ratio of the amount of oxygen loss to the amount of reduction gas should be adopted to display the utilization rate of reduction gas. In the reduction stage of Fe_{0.95}O \rightarrow Fe, the utilization rate does not change with the increase of the deoxygenation rate of Fe₂O₃. Therefore, this rule can be used to calculate the reduction gas utilization rate under different settings, such as gas concentration, gas pressure, etc.

Figure 2d shows the CH₄ conversion rate with increasing the amount of initial reduction gas at the current setting. In the reduction stage of Fe_{0.95}O \rightarrow Fe, the CH₄ conversion rate remains unchanged with the increase of the reduction gas. The increased CH₄ has reacted with the increased H₂O and CO₂ obtained from the reduction of Fe_{0.95}O, which is shown in Figure 2a. At any reduction stage of iron oxide, CH₄ is almost completely decomposed, and the conversion rate of CH₄ is ≥99.982%. When the amount of reduction gas is more than needed, the CH₄ conversion rate decreases rapidly, and the reason is that the amount of CO₂ and H₂O generated from the reduction of iron oxide do not increase.

3.2. The Utilization Rate of Reduction Gas

The utilization rate of reduction gas for the full reduction of iron oxide is the same as that of the partial reduction stage of $Fe_{0.95}O \rightarrow Fe$. Therefore, the initial amount of reduction gas is set as 2 mol. The initial gas concentration is $H_2\% + CO\% = 90$, $CH_4\% = 0-10$, the residual is N_2 , and these given initial gas concentration (volume fraction) are listed in Table 3. The total pressure is 1–9 atm and the reaction temperature is 900 °C.

The Figure 3a,b show the relationship between the utilization rate of total gas and the total gas pressure, and the former fixes the initial concentrations of both H₂ and CO at 45%, the latter fixed the initial concentration of CH₄ at 2%. As can be seen from these two figures, no matter what the initial gas concentration is, the gas utilization rate decreases with the increase of the total gas pressure, expect for single gas reduction. However, the influence of pressure on the gas utilization rate is not significant. The change of gas utilization rate from 1 atm to 9 atm is less than 1.70%, as shown in Figure 4. Also, when initial H₂% = 60, the pressure has the greatest effect on gas utilization, which is close to 1.70%.



Figure 3. The relationship between the utilization rate of total gas and other initial conditions at 900 °C. (a) the *x*-axis is the total gas pressure, and initial $H_2\% = 45$, CO% = 45, $CH_4\% = 0$ –10; (b) *x*-axis is the total gas pressure, and initial $H_2\% + CO\% = 90$, $CH_4\% = 2$; (c) *x*-axis is the initial CH_4 volume fraction, and initial $H_2\% = 45$, CO% = 45; (d) *x*-axis is the total gas pressure, and initial $H_2\% + CO\% = 90$, $CH_4\% = 2$; evaluate of the initial $H_2\% + CO\% = 90$, $CH_4\% = 2$.

Figure 3c shows the relationship between the utilization rate of total gas and the initial CH_4 volume fraction. It can be seen from these two figures, no matter what the initial gas concentration is, the gas utilization rate decreases with the increase of the total gas pressure. In other words, increasing the concentration of CH_4 can greatly improve the gas utilization rate. Besides, the lines under different pressures are nearly parallel. According to the calculation of the slope, for every 1% increase in CH_4 concentration, the gas utilization rate can be improved by 2.03–2.07%.

Figure 3d shows the relationship between the utilization rate of total gas and the initial H₂ volume fraction. As can be seen from the figure, the gas utilization rate increases as the initial H₂ concentration increases also decreases as the initial CO concentration increases. Also, the two ends of all curves are approximately coincident, that is, when the gas concentration is (H₂% = 90, CH₄% = 2) and (CO% = 90, CH₄% = 2), the pressure has little effect on the gas utilization. For other H₂ concentrations, the higher the pressure is, the lower the utilization of the gas is. Based on the slope calculation, every 1% increase in H₂ concentration can improve the gas utilization rate by about 0.06%.



Figure 4. The relationship between the rangeability of the utilization rate of total gas at 900 $^{\circ}$ C and the initial H₂ volume fraction.

Table 4 lists the utilization rate of total gas of the selected nine groups of gas concentrations under different pressure. For single reduction gas (CO% = 90, N₂% = 10) and (H₂% = 90, N₂% = 10), the utilization rate of total gas at 900 °C is 28.305% and 33.823%, respectively. Increasing CH₄ concentration and decreasing the pressure can improve the gas utilization rate. At the same temperature and pressure, pure H₂ has the highest gas utilization rate, while pure CO has the lowest gas utilization rate.

Initial Gas Concentration/%			Total Gas Pressure/Atm								
H ₂	СО	CH ₄	1	2	3	4	5	6	7	8	9
0	90	0	28.305	28.305	28.305	28.305	28.305	28.305	28.305	28.305	28.305
0	90	2	32.438	32.437	32.436	32.435	32.435	32.434	32.433	32.431	32.430
0	90	5	38.635	38.633	38.631	38.627	38.623	38.617	38.611	38.603	38.595
45	45	0	31.058	31.040	31.011	30.971	30.919	30.855	30.78	30.695	30.598
45	45	2	35.189	35.169	35.136	35.089	35.030	34.957	34.872	34.774	34.663
45	45	5	41.386	41.362	41.322	41.267	41.195	41.108	41.006	40.889	40.757
90	0	0	33.823	33.823	33.823	33.823	33.823	33.823	33.823	33.823	33.823
90	0	2	37.954	37.951	37.946	37.938	37.929	37.918	37.904	37.889	37.872
90	0	5	44.151	44.143	44.130	44.111	44.088	44.059	44.025	43.987	43.943

 Table 4. The utilization rate of total gas of the selected nine groups of gas concentration under different pressure.

3.3. The Saving Volume of Reduction Gas per m^3 CH₄

The reduction gas needed for the full reduction of iron oxide to produce 1 ton of metallic Fe can be calculated by the utilization rate of reduction gas. For $H_2\% = 45$, CO% = 45, $CH_4\% = 0$ –10, gas pressure is 1–9 atm, the reduction gas required for a ton of iron is shown in Figure 5. As can be seen from Figure 5, the amount of reduction gas required per ton of iron decreases with the increase of CH₄ content. For example, when the initial CH₄% is 0, the reduction gas ($H_2\% = 45$, CO%45, $N_2\% = 10$, gas pressure 4 atm) needed is 1937.319 m³; when the initial CH₄% is 5, that is 1453.959 m³, the reduction gas required decreases by 483.36 m³.



Figure 5. The relationship between the volume for total gas needed for per ton Fe and initial CH₄ volume fraction at 900 °C with the initial H₂% = 45 and CO% = 45 under 1–9 atm.

The reduction gas demand can be saved by increasing CH₄ into the mixture, and the specific effect can be calculated by Formula (30), which is shown in Figure 6. As can be seen from the figure, the saving effect decreases with the increase of the initial CH₄ concentration, and the decreasing trend is obvious with the increase of the pressure. However, the range of these savings due to pressure and CH₄ concentration is small, with a maximum of just 0.008 m³/m³. Therefore, it can be considered that for reduction gas (H₂% = 45, CO% = 45, N₂% = 10, and the pressure is 1–9 atm), 1 m³ CH₄ can save 6.64–6.65 m³ total reduction gas.



Figure 6. The relationship between the saving volume per m³ CH₄ and initial CH₄ volume fraction at 900 °C with the initial H₂% = 45 and CO% = 45 under 1–9 atm.

Figure 7 shows the relationship between saving volume of total gas per m³ CH₄ and the initial H₂ concentration. It can be seen from Figure 7 that the saving volume per m³ CH₄ decreases linearly with the increase of the initial H₂ concentration. Since CH₄ concentration has little influence on the savings effect of CH₄, the points in Figure 7 are coincide, and the coordinate values of the main nodes have been marked in the figure. For gas concentration from (H₂% = 0, CO% = 90) to (H₂% = 90, CO% = 0), the saving effect of CH₄ is decreased from 7.29 m³/m³ to 6.08 m³/m³. Compared with pressure and CH₄ concentration, H₂ concentration has a more significant effect on the savings effect of CH₄.



Figure 7. The relationship between the saving volume per m^3 CH₄ and initial H₂ volume fraction at 900 °C under 4 atm.

It is important to note that the volume saving per m^3 CH₄ cannot be calculated according to Formula (9) and (10). According to Formula (9), the reaction between CH₄ and H₂O can produce $3 m^3 H_2 + 1 m^3$ CO by $1 m^3$ CH₄. According to Formula (10), the reaction between CH₄ and CO₂ can get $2 m^3 H_2 + 2 m^3$ CO by $1 m^3$ CH₄. In other words, the reaction of CH₄ with deoxidized products H₂O and CO₂ results in a mixture of $4 m^3 H_2 + CO$. However, this algorithm for saving effect without the iron oxide reduction system is not correct, due to the gas utilization rate for reduction is neglected. In the gas system composed of CH₄ + H₂O + H₂ + CO₂ + CO, five kinds of gases. H₂O + H₂, and CO₂ + CO are also in equilibrium.

The reaction enthalpy of reduction of iron oxide can be calculated by Formula (24). Figure 8 shows the relationship between the reaction enthalpy and the initial gas amount, and the oblique line shows the full reduction of iron oxide. The curve that demonstrates the reduction by gas without CH_4 is at the bottom of all curves and reaches a maximum value of 8.3 kJ/mol when the iron oxide is completely reduced; due to reverse reaction of Formulas (9) and (10), the curve starts to go down. For the reduction by gas included CH_4 , the reaction enthalpy increases with the increase of the amount of reduction gas.



Figure 8. The relationship between the reaction enthalpy and the initial gas amount at 900 °C under 4 atm with H_2 % = 45, CO% = 45, CH₄% = 0–10.

Figure 9 shows the relationship between the reaction enthalpy and the initial CH_4 concentration. As shown in the figure, reaction enthalpy is linearly correlated with the initial CH_4 concentration. The initial reduction gas volume is set as 1.5 mol, 2.0 mol, and 2.5 mol, respectively, so the equilibrium state is in the stage of $Fe_{0.95}O \rightarrow Fe$. According to the calculation by Formula (33), the change of reaction enthalpy brought by 1 mol CH_4 is the same at the same pressure. Increasing the pressure can reduce the change value of reaction enthalpy. The change of reaction enthalpy caused by 1 mol CH_4 at 4 atm, 5 atm, and 6 atm is 249.79 kJ/mol, 249.31 kJ/mol, and 248.72 kJ/mol, respectively.

$$\Delta H_{1173K} = \frac{\text{slope of reaction enthalpy}}{\text{increment of the initial amount of CH}_4}$$
(33)



Figure 9. The relationship between the reaction enthalpy and the initial CH₄ volume fraction at 900 °C with $H_2\% = 45$, CO% = 45. (a) the total pressure is 4 atm; (b) total pressure is 5 atm; (c) total pressure is 6 atm.

3.5. The Increased Reaction Enthalpy Per m^3 CH₄

Comparing the reduction of iron oxide by gas within CH_4 and by gas without CH_4 , the reaction enthalpy increases under the same initial concentration of H_2 and CO and pressure.

Figure 10 shows the relationship between the increased reaction enthalpy per m³ CH₄ and the total gas pressure and the initial H₂ concentration. As shown in the figure, the increased reaction enthalpy decreases with the increase of the total gas pressure, or with the increase of the initial H₂ concentration. For the gas (H₂% = 0, CO% = 90, the pressure is 1atm), the increased reaction enthalpy per m³ CH₄ is the maximum of 11.189 MJ/m³. For the gas (H₂% = 90, CO% = 0, the pressure is 9atm) the increased reaction enthalpy per m³ CH₄ is the smallest of 10.959 MJ/m³.



Figure 10. The increased reaction enthalpy per m³ CH₄ at 900 with H₂% + CO% = 90. (**a**) the *x*-axis is the total gas pressure; (**b**) *x*-axis is the initial H₂ volume fraction.

For the gas ($H_2\% = 0$, CO% = 90, $N_2\% = 10$), the reaction enthalpy for producing a ton of iron is -330.280 MJ. For the gas ($H_2\% = 90$, CO% = 0, $N_2\% = 10$), and the reaction enthalpy for the production of a ton of iron is 568.471 MJ. The addition of 30 m³ CH₄ in the gas phase can make the reaction enthalpy of the former gas system zero, and the latter gas system more heat supply needed.

According to the reduction reaction and methane conversion reaction, the reaction between CH_4 and iron oxide is obtained by coupling, as shown in Formulas (34) and (35). The released heat of chemical reaction in the production of 1 mol of Fe with CO is 18.445 kJ, the absorption heat of chemical reaction in the production of 1 mol of Fe with H_2 is 31.747 kJ, and the absorption heat of chemical reaction in the production of 1 mol of Fe with CH_4 is 373.061 kJ.

$$Fe_{2}O_{3} + 3CO = 2Fe + 3CO_{2} \qquad \Delta H^{\ominus}_{1173K} = -36.890 \text{ kJ/mol} \\ + 3 \times (CH_{4} + CO_{2} = 2H_{2} + 2CO) \qquad \Delta H^{\ominus}_{1173K} = 261.004 \text{ kJ/mol}$$
(34)

$$Fe_{2}O_{3} + 3CH_{4} = 2Fe + 6H_{2} + 3CO \qquad \Delta H^{\ominus}_{1173K} = 746.121 \text{ kJ/mol}$$
(34)

$$\begin{array}{rcl} Fe_{2}O_{3} + 3H_{2} &=& 2Fe + 3H_{2}O \\ +3 \times (CH_{4} + H_{2}O = 3H_{2} + CO) \\ Fe_{2}O_{3} + 3CH_{4} &=& 2Fe + 6H_{2} + 3CO \end{array} \qquad \begin{array}{l} \Delta H_{1173K}^{\ominus} &=& 63.495 \text{ kJ/mol} \\ \Delta H_{1173K}^{\ominus} &=& 227.542 \text{ kJ/mol} \\ \Delta H_{1173K}^{\ominus} &=& 746.121 \text{ kJ/mol} \end{array}$$
(35)

When the initial CH_4 concentration is set to be 10% at most, the amount of CO_2 and H_2O in the system are excessive relative to that of CH_4 ; that is, the conversion reaction of CH_4 is relatively sufficient, as shown in Figure 2d. When the initial concentration of CO and H_2 in the gas phase changes, the concentration of CO_2 and H_2O generated by the reduction reaction also changes along with it, thus making the reaction enthalpy of CH_4 conversion different. The reduction utilization rate of H_2 is higher than that of CO at 900 °C. Increasing the initial H_2 concentration can increase the overall gas utilization rate and the concentration of H_2O in the gas phase. In addition, the reaction enthalpy of $H_2O + CH_4$ is lower than that of $CO_2 + CH_4$, which reduces the increased reaction enthalpy of the system.

The transformation reaction of CH_4 are reactions in which the amount of substance increases. Increasing the gas pressure can decrease the amount of forwarding reaction and the gas utilization rate, which lowers the increased reaction enthalpy of the system.

3.6. The Heat Needed per Ton Fe

The total heat needed of reduction of iron oxide by gas at 900 °C consists of three parts: reaction heat, the sensible heat of solid Fe_2O_3 from 25 °C to 900 °C, and sensible heat of gas mixture from 25 °C to 900 °C. MJ/tFe represents heat unit per ton Fe.

Figure 11 shows the relationship between reduced sensible heat of reduction gas and CH_4 concentration, gas pressure, and H_2 concentration, which is compared with the reduction without CH_4 . As can be seen from Figure 11a, the reduced sensible heat of reduction gas increases with the increase of CH_4 concentration and has little been influenced by the gas pressure in the range of 1–9 atm. As can be seen from Figure 11b, under the same gas pressure and CH_4 concentration, the reduced sensible heat of reduction gas decreases with the increase of H_2 concentration.



Figure 11. The relationship between the reduced sensible heat of total gas and the initial CH₄ volume fraction at 900 °C. (a) $H_2\% = 45$, CO% = 45, total pressure is 1–9 atm; (b) $H_2\% + CO\% = 90$, total pressure is 4 atm.

In addition, according to the sensible heat calculation Formula (24) and gas composition, it can be obtained that the saved sensible heat of gas per m³ CH₄ is 7.338–8.952 MJ. The former corresponds to gas mixture H₂% = 90, CO% = 00, CH₄% + N₂% = 10, and gas pressure = 9atm. The latter corresponds to gas mixture H₂% = 0, CO% = 90, CH₄% + N₂% = 10, and gas pressure = 1atm.

Figure 12 shows the relationship between increased reaction heat and CH_4 concentration, gas pressure, and H_2 concentration, which is compared with the reduction without CH_4 . As can be seen from Figure 12a, the increased reaction heat goes up with the increase of CH_4 concentration and has been little influenced by the gas pressure in the range of 1–9atm. As can be seen from Figure 12b, under the same gas pressure and CH_4 concentration, the increased reaction heat decreases with the increase of H_2 concentration.



Figure 12. The relationship between the increased reaction heat and the initial CH₄ volume fraction at 900 °C. (a) $H_2\% = 45$, CO% = 45, total pressure is 1–9 atm; (b) $H_2\% + CO\% = 90$, total pressure is 4 atm.

The sensible heat of the solid Fe_2O_3 is 1123.381 MJ/tFe, which is a constant under certain temperature change conditions. Therefore, increased total heat can be defined by the difference of gas sensible heat and reaction heat, as shown in Formula (36).

increased total heat
$$=$$
 increased reaction heat $-$ reduced gas sensible heat (36)

The relationship between increased total heat with CH_4 concentration, gas pressure, and H_2 concentration is shown in Figure 13. It can be seen that the increased total heat increases with the increase of CH_4 concentration, and has been little influenced by the gas pressure in the range of 1–9 atm. As can be seen from Figure 13b, under the same gas pressure and CH_4 concentration, the increased reaction heat increases with the increase of H_2 concentration.



Figure 13. The relationship between the increased total heat and the initial CH₄ volume fraction at 900 °C. (a) $H_2\% = 45$, CO% = 45, total pressure is 1–9 atm; (b) $H_2\% + CO\% = 90$, total pressure is 4 atm.

According to Formula (36), increasing 1 m³ CH₄ can increase the total heat by 2.174–3.703 MJ. The former corresponds to gas mixture $H_2\% = 0$, CO% = 90, $CH_4\% = 1$, $N_2\% = 9$, and gas pressure = 9 atm. The latter corresponds to gas mixture $H_2\% = 90$, CO% = 0, $CH_4\% = 1$, $N_2\% = 9$, and gas pressure = 1 atm.

Figure 14 shows the relationship between the total heat and CH₄ concentration, gas pressure, and H₂ concentration, and its variation trend is the same as that of the increased total heat. Taking the reduction by H₂% = 45, CO% = 45, CH₄% = 0, N₂% = 10 gas mixture as an example, as shown in Figure 14a, the total heat needed is 3649.223 MJ/tFe (gas pressure = 1 atm) and 3636.249 MJ/tFe (gas pressure = 9 atm), and the slight difference is due to the lower reaction heat caused by the increase in pressure. When the gas pressure = 4 atm, as shown in Figure 14b, the total heat needed is 3865.76 MJ/tFe for the reduction by H₂% = 0, CO% = 90, CH₄% = 0, N₂% = 10 gas mixture and 3390.828 MJ/tFe for the reduction by H₂% = 90, CO% = 0, CH₄% = 0, N₂% = 10 gas mixture, and the huge difference is due to the exothermic reaction of CO + Fe₂O₃.



Figure 14. The relationship between the total heat and the initial CH₄ volume fraction at 900 °C. (a) $H_2\% = 45$, CO% = 45, total pressure is 1–9 atm; (b) $H_2\% + CO\% = 90$, total pressure is 4 atm.

The maximum increase rate in total heat caused by the presence of CH₄ is 10.582% (H₂% = 90, CH₄% =10, gas pressure = 1 atm) compared to the reducing gas without CH₄. An appropriate increase in total heat is acceptable since it saves the amount of H₂ + CO and reduces the purity limit of H₂ + CO. However, the addition of CH₄ requires more heat supply for gas reduction and may increase the carbon content.

4. Conclusions

The minimum free energy method was used to calculate the equilibrium state composition of the reduction of iron oxide by gas with $H_2\% + CO\% = 90$ and $CH_4\% + N_2\% = 10$ at 900 °C under 1–9 atm, and the following conclusions were obtained:

- (1) Increasing CH₄ concentration, increasing H₂ concentration, or reducing gas pressure can improve the utilization rate of total gas, reduce the reduction gas demand, and increase the total heat needed.
- (2) Under the condition of 900 °C and 1–9 atm, increasing 1 m³ CH₄ can reduce the gas demand of 6.08–7.29 m³, the gas sensible heat needed to be 7.338–8.952 MJ, and the increase in the reaction heat needed to be 10.959–11.189 MJ.
- (3) Compared with 3390.828–3865.760 MJ of the total heat of per ton Fe for the reduction by $H_2 + CO$, increasing 1 m³ CH₄ can increase the total heat by 2.174–3.703 MJ, and increase ratio is 0.065–0.096%.

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