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Thermodynamic Calculation on the Reduction of Iron Oxide in an H_2 Atmosphere

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Abstract

Thermodynamic calculation on the reduction of iron oxide in H_2 atmosphere is carried out in this paper. The general calculation model of the standard free energy changes for reactions are established. Accurate calculation and plotting of the standard free energy changes, equilibrium constants and gas composition for preparing iron by reduction of iron oxide in H_2 atmosphere are realized using the developed general computer program.

Keywords: Equilibrium constant, computational thermodynamics, chemical equilibrium, chemical reduction, ironoxide, H_2-atmosphere

1. Introduction

The thermodynamic study of the phase equilibria during chemical reactions provides a basic understanding of the process prior to designing suitable reaction experiments, and therefore provides a useful guideline for the selection of processing conditions. Prior to chemical reactions, it is essential to determine the feasibility of the chemical reactions, and the nature and amount of the solid and gaseous species present in the system. These can be determined from the calculation of the thermodynamic equilibrium (i.e. the equilibrium partial pressures of the system species) at a given set of processing conditions such as reaction temperature, pressure and reactant concentration (Choy, 2003). It is known that the calculation and plotting of standard Gibbs free energy changes for reactions are important thermodynamics content in many courses such as materials science, metallurgy principles and physical chemistry. It is significant for using the value of standard free energy changes to approximately analyze the trends of substances reactions and phases transitions in chemical reactions, metallurgy processes, materials synthesis and processing (Mattigod and McGrail, 1999; Chattorraj et al., 1996; Jayaram et al., 1999; Alberty, 2004). Moreover at equilibrium the equilibrium constant can be gained by linking to the value of the standard free energy change for the reaction. However it is not easy to accurately calculate and plot the standard free energy changes and equilibrium constants for reactions due to the calculation complexity of reactions and phase transitions. It is found in the literature (Li, 2001) that it is not simple and convenient for calculation of standard free energy changes for reactions using the computer program, because the polynomial integral operation, plotting and calculating of the equilibrium constant are not included in the computer program, which makes the calculation results imprecise. At present it has not been found in the literature for accurate calculation and plotting of the standard free energy changes and the equilibrium constant for reactions using the general computer program. Iron powders can be prepared in production by reduction of iron oxide powders in H_2 atmosphere. Taking the reduction of iron oxide powders in H_2 atmosphere as an example, the purpose of the study is to develop the calculation and plotting model of the standard Gibbs free energy changes for chemical reactions, and to accurately calculate and plot the standard free energy changes, the equilibrium constants and gas composition for most reactions and phase transformations only inputing the basic thermodynamic data tabulated in data books into the computer program.

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2. Calculation Model of the Standard Free Energy of Reactions

The chemical reactions for preparing iron powders by reduction of iron oxide powders in H_2 atmosphere are dependent with the reaction temperature.

When the reduction temperature is higher than a certain temperature, following three reactions will occur:

$$3Fe_2O_{3(s)} + H_{2(g)} = 2Fe_3O_{4(s)} + H_2O_{(g)} \qquad (1)$$

$$Fe_3O_{4(s)} + H_{2(g)} = 3FeO_{(s)} + H_2O_{(g)} \qquad (2)$$

$$FeO_{(s)} + H_{2(g)} = Fe_{(s)} + H_2O_{(g)} \qquad (3)$$

When the reduction temperature is below a certain temperature, Fe_3O_4 will be reduced directly as Fe:

$$Fe_3O_{4(s)} + 4H_{2(g)} = 3Fe_{(s)} + 4H_2O_{(g)} \qquad (4)$$

Usually a multiple reaction can replace the above reactions, and can be expressed below:

$$xA+yB+zC+wD = uE+vF+pG+qH \qquad (5)$$

where A, B, C, D, E, F, G, and H denote each substance in the reaction, respectively; x, y, z, w, u, v, p, and q representing the each substance mole in the reaction, respectively.

Taking reaction (1) as an example, each substance and mole in the reaction are below:

x=3, y=1, z=0, w=0, u=2, v=1, p=0, q=0, A= Fe_2O_3, B= H_2, C= 0, D=0, E= Fe_3O_4, F= H_2O, G= 0, H=0.

The standard free energy of reactions $\Delta_r G^0$ is described as:

$$\Delta_r G^0 = \sum nG_f^0 \text{(products)} - \sum mG_f^0 \text{(reactants)} \qquad (6)$$

where n and m represent the moles of each product and reactant given by the coefficient in the balanced chemical equation, respectively; $\sum nG_f^0$ (products) and $\sum mG_f^0$ (reactants) represent the sum of the changes in the standard free energy of formation for each product and reactant, respectively. That is (Pavel, 2000, Kubatevsky and Aolkaok, 1985)

$$\Delta_r G^0 = \Delta_f H^0_{298} + \int_{298}^{T} \Delta C_p \, dT - T\Delta_r S^0_{298}$$

$$- T\int_{298}^{T} \frac{\Delta C_p}{T} \, dT \qquad (7)$$

where $\Delta_f H^0_{298}$ and $\Delta_r S^0_{298}$ denote the changes for the standard enthalpy of formation and the standard entropy of reaction for each product or reactant at 298K in the reaction, respectively; T is the temperature in Kelvin; ΔC_p is the change of the (molar) heat capacity at constant pressure for each product or reactant; C_P is the (molar) heat capacity at constant pressure. It is possible to express the heat capacity as (Pavel, 2000, Kubatevsky and Aolkaok, 1985):

$$C_P = a+bT+cT^{-2}+eT^2 \qquad (8)$$

where a, b, c and e are the heat capacity coefficients often tabulated in data books.

According to the reaction (5) and equation (7), the calculation model is constructed as follows:

$$\begin{aligned}\Delta_f H^0_{298} = {} & u\Delta_f H^0_{298}(E) + v\Delta_f H^0_{298}(F) \\ & + p\Delta_f H^0_{298}(G) + q\Delta_f H^0_{298}(H) \\ & - x\Delta_f H^0_{298}(A) - y\Delta_f H^0_{298}(B) \\ & - z\Delta_f H^0_{298}(C) - w\Delta_f H^0_{298}(D),\end{aligned} \qquad (9)$$

$$\begin{aligned}\Delta_r S^0_{298} = {} & u S^0_{298}(E) + v S^0_{298}(F) \\ & + p S^0_{298}(G) + q S^0_{298}(H) \\ & - x S^0_{298}(A) - y S^0_{298}(B) \\ & - z S^0_{298}(C) - w S^0_{298}(D),\end{aligned} \qquad (10)$$

where $\Delta_f H^0_{298}$ (E), $\Delta_f H^0_{298}$ (F), $\Delta_f H^0_{298}$ (G), $\Delta_f H^0_{298}$ (H), $\Delta_f H^0_{298}$ (A), $\Delta_f H^0_{298}$ (B), $\Delta_f H^0_{298}$ (C), $\Delta_f H^0_{298}$ (D), S^0_{298} (E), S^0_{298} (F), S^0_{298} (G), S^0_{298} (H), S^0_{298}(A), S^0_{298}(B), S^0_{298}(C) and S^0_{298}(D) represent the enthalpy of formation and standard entropy for each product and reactant at 298 K in the reaction, respectively.

$$\begin{aligned}\Delta C_p = {} & u\,C_P(E) + v\,C_P(F) + p\,C_P(G) + q\,C_P(H) \\ & - x\,C_P(A) - y\,C_P(B) - z\,C_P(C) - w\,C_P(D) \\ = {} & u\,(a(E) + b(E)T + c(E)T^{-2} + d(E)T^3 + e(E)T^2) \\ & + v\,(a(F) + b(F)T + c(F)T^{-2} + d(F)T^3 + e(F)T^2) \\ & + p(a(G) + b(G)T + c(G)T^{-2} + d(G)T^3 + e(G)T^2) \\ & + q(a(H) + b(H)T + c(H)T^{-2} + d(H)T^3 + e(H)T^2) \\ & - x(a(A) + b(A)T + c(A)T^{-2} + d(A)T^3 + e(A)T^2) \\ & - y(a(B) + b(B)T + c(B)T^{-2} + d(B)T^3 + e(B)T^2) \\ & - z(a(C) + b(C)T + c(C)T^{-2} + d(C)T^3 + e(C)T^2) \\ & - w(a(D) + b(D)T + c(D)T^{-2} + d(D)T^3 + e(D)T^2)\end{aligned} \qquad (11)$$

where each letter and sign correspond with the components or coefficients in the above reactions and equations, respectively.

According to the Gibbs equation as follows:

$$\Delta_r G = \Delta_r G^0 + RT \ln K^0 \qquad (12)$$

At equilibrium there is no net driving force for the reaction, the reaction will not proceed spontaneously either forward or backward, so

$\Delta_r G$ is zero. That is

$$\Delta_r G^0 = -RT \ln K^0$$

or

$$\Delta_r G^0 = -2.303\, RT \lg K^0 \qquad (13)$$

where R is the ideal gas law constant, 8.314 (J/mol·K); K^0 is the equilibrium constant for the chemical equilibrium taking place; ln and lg represent the logarithm to the base e and 10, respectively. K^0 = multiple of product activities (or partial pressure) = multiple of gaseous reactant activities (or partial pressure).

In the reduction reactions of iron oxide powders in H_2 atmosphere, K_p p_{H2O} / p_{H2}; p_{H2O} and p_{H2} are partial pressures of H_2O and H_2, respectively; $p_{H2O} + p_{H2} = 1$ atm.; $H_2\% = p_{H2} \times 100$.

It is noticeable that the heat capacity coefficients for some substances possess different values during the different temperature ranges, therefore when calculating the sections of $\int_{298}^{T} \Delta C_p \, dT$ and $\int_{298}^{T} \frac{\Delta C_p}{T} dT$ in $\Delta_r G^0$ the following subsection integral formula must be used in the program:

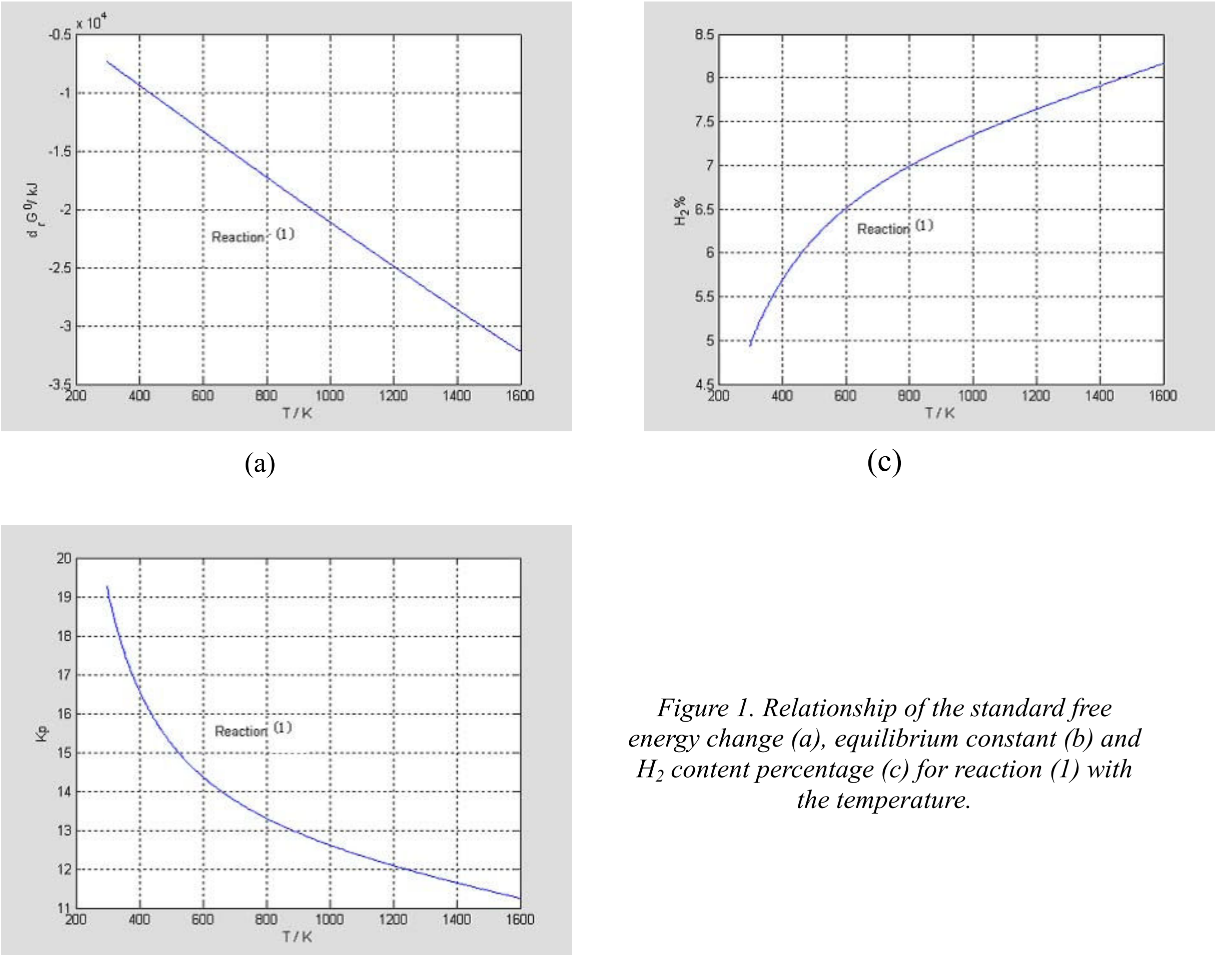
$$\int_a^c f(T)dT = \int_a^b f(T)dT + \int_b^c f(T)dT \qquad (14)$$

3. Results of Calculation and Plotting

The general computer program of calculation and plotting for standard free energy changes, equilibrium constants and gas composition for the reactions has been developed using the above model. The thermodynamic data for the substances in the reaction (1), (2), (3) and (4) are listed in TABLE I (http://www.sdb.ac.cn/), the results of the calculation and plotting for the standard free energy changes and the equilibrium constants for the reaction (1), (2), (3) and (4) using the developed computer program are shown in *Figures 1, 2, 3 and 4*, respectively.

TABLE I. THERMODYNAMIC DATA OF THE SUBSTANCES IN THE REACTIONS.

Substance	ΔH^0_{298}, kJ/mol	S^0_{298}, J/(mol·K)	C_P, J/(mol·K)				Temperature range, K
			a	b x10^{-3}	c x10^{5}	e x10^{-6}	
$Fe_2O_{3\,(s)}$	-197.3	20.9	23.49	18.6	-3.55	0	298-953
			36	0	0	0	953-1050
			31.71	1.76	0	0	1050-1735
$H_{2(g)}$	0	31.233	4.044	14.089	0.141	-19.015	298-400
			6.759	0.1	0.196	0.351	400-1600
$Fe_3O_{4\,(s)}$	-267.3	35	20.618	49.932	0	0	298-866
			48	0	0	0	866-1870
$H_2O_{(g)}$	-57.798	45.1322	8.023	-1.004	0	3.528	298-600
			5.227	5.392	2.029	-0.956	600-1600
$FeO_{(s)}$	-65.02	14.52	12.142	2.059	-0.791	0	298-1650
$Fe_{(s)}$	0.215	6.52	6.734	-1.749	-0.692	5.985	298-800
			-62.967	61.14	148	0	800-1000
			-153.419	166.429	0	0	1000-1042
			465.166	-427.222	0	0	1042-1060
			-134.305	79.862	696.012	0	1060-1184
			5.734	1.998	0	0	1184-1665

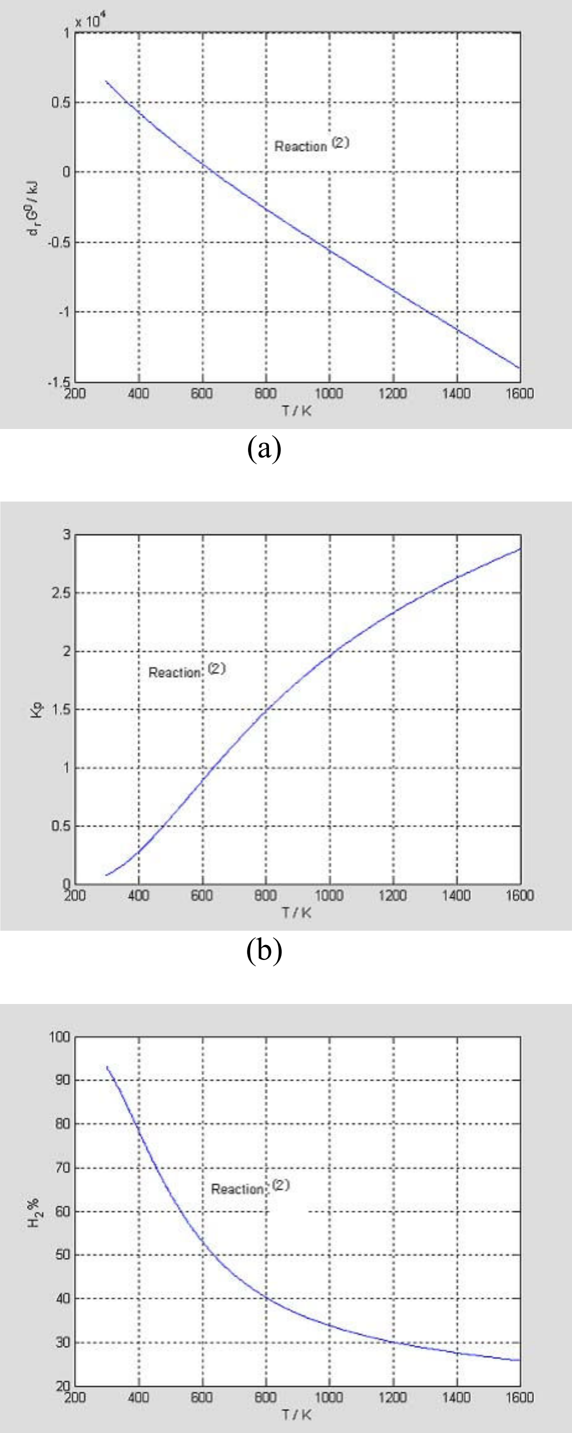


(a)

(c)

(b)

Figure 1. Relationship of the standard free energy change (a), equilibrium constant (b) and H_2 content percentage (c) for reaction (1) with the temperature.

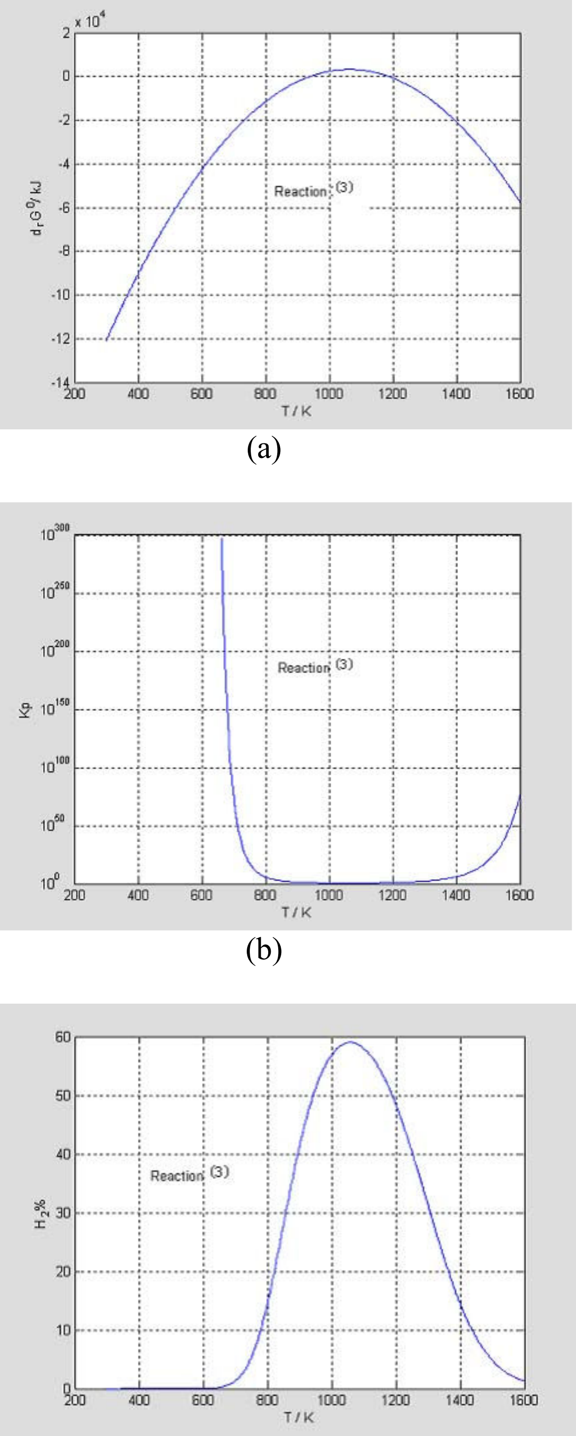


(a)

(b)

(c)

Figure 2. Relationship of the standard free energy change (a), equilibrium constant (b) and H_2 content percentage (c) for reaction (2) with the temperature.

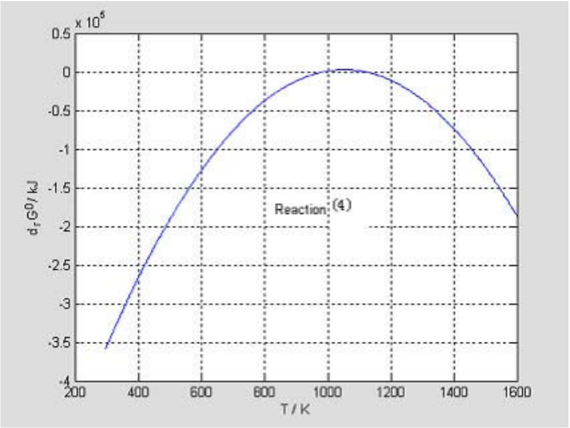


(a)

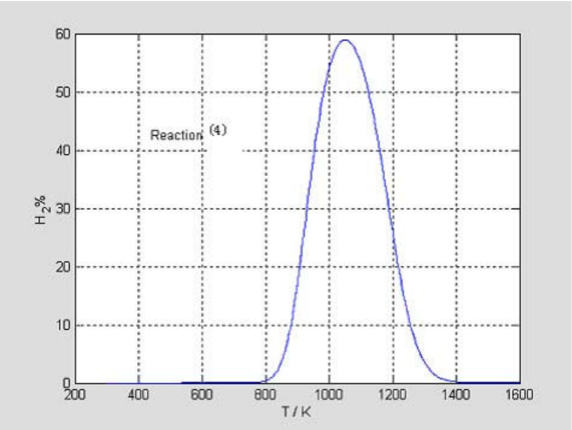
(b)

(c)

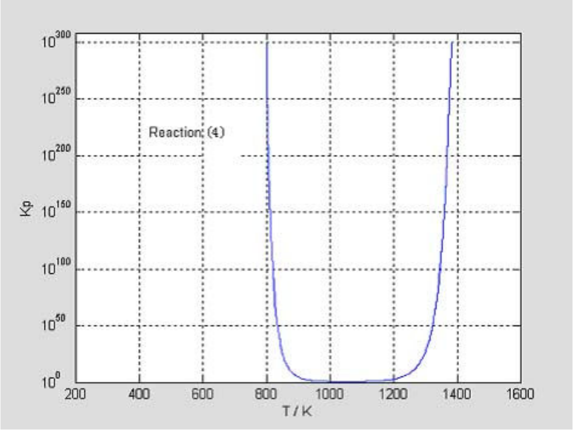
Figure 3. Relationship of the standard free energy change (a), equilibrium constant (b) and H_2 content percentage (c) for reaction (3) with the temperature.



(a)



(c)



(b)

Figure 4. Relationship of the standard free energy change (a), equilibrium constant (b) and H_2 content percentage (c) for reaction (4) with the temperature.

It is shown from the above figures that the relationships of the standard free energy changes for reactions (1), (2), (3) and (4) when the temperatures are not so well in accordance with the linear change that is the general calculation results for most Chinese literature in which most C_P values are ignored (Li, 2001). It is easy and quick to accurately calculate and plot the standard free energy changes, equilibrium constants for reactions, only inputting the basic thermodynamic data tabulated in data books into the computer program.

4. Conclusion

This paper presents the thermodynamic calculation on reduction of iron oxide in H_2 atmosphere. Accurate calculation and plotting of the standard free energy changes, equilibrium constants and gas composition for preparing iron by reduction of iron oxide in H_2 atmosphere are realized using the developed general computer program. The results show that the relationships of the standard free energy changes for the reactions with the temperatures are not so good in accordance with the linear change that are the general calculation results for most Chinese literature in which most C_P values are ignored. Moreover the developed general computer program can be used for calculation and plotting of the standard Gibbs free energy changes and equilibrium constants for most reactions and phase transitions in chemical reactions, metallurgy processes, materials synthesis and processing, only inputing the basic thermodynamic data tabulated in data books into the computer program.

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