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Thermodynamic calculation on reduction of tungsten oxide in H_2 atmosphere

Liu Sha [a,*], Zhang Jing Qiu [b]

[a] School of Materials Science and Engineering, Central South University, Changsha, Hunan 410083, PR China
[b] Institute of Information Science and Engineering, Central South University, Changsha, Hunan 410083, PR China

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Abstract

Thermodynamic calculation on reduction of tungsten 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 tungsten by reduction of tungsten oxide in H_2 atmosphere are realized using the developed general computer program, especially for the polynomial integral and subsection integral operations.

Keywords: Thermodynamics; Calculation and plotting; Chemical reaction; Tungsten oxide

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 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, 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 [1]. It is known that calculation and plotting of standard Gibbs free energy changes for reactions are important thermodynamics content in many courses such as materials science, metallurgy principle, physical chemistry and so on. It is theoretically 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 [2–5]. Moreover at chemical 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 [6] 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 literatures for accurate calculation and plotting of the standard free energy changes and the equilibrium constant for reactions using the general computer program, especially for polynomial integral and subsection integral operations. Tungsten powders are mainly prepared in production by reduction of tungsten oxide powders in H_2 atmosphere. Taking the reduction of tungsten oxide powders in H_2 atmosphere as an example, the purpose of the study is to establish the calculation and plotting model of the standard Gibbs free energy changes for chemical reactions, and to accurately

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* Corresponding author.
E-mail address: liusha90@yahoo.com.cn (L. Sha).

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calculate and plot the standard free energy changes, the equilibrium constants and gas composition for most reactions and phase transformations only inputting the basic thermodynamic data tabulated in data books into the computer program.

2. Calculation model of the standard free energy of reactions

Tungsten powders are mainly prepared in production by reduction of tungsten oxide powders in H_2 atmosphere. The main chemical reactions for preparing tungsten powders by reduction of tungsten oxide powders in H_2 atmosphere are as following:

$$WO_{3(s)} + 0.1H_{2(g)} = WO_{2.9(s)} + 0.1H_2O_{(g)} \tag{1}$$

$$WO_{2.9(s)} + 0.18H_{2(g)} = WO_{2.72(s)} + 0.18H_2O_{(g)} \tag{2}$$

$$WO_{2.72(s)} + 0.72H_{2(g)} = WO_{2(s)} + 0.72H_2O_{(g)} \tag{3}$$

$$WO_{2(s)} + 2H_{2(g)} = W_{(s)} + 2H_2O_{(g)} \tag{4}$$

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

$$x\mathrm{A} + y\mathrm{B} + z\mathrm{C} + w\mathrm{D} = u\mathrm{E} + v\mathrm{F} + p\mathrm{G} + q\mathrm{H} \tag{5}$$

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

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

$$x = 1,\ y = 0.1,\ z = 0,\ w = 0,\ u = 1,\ v = 0.1,\ p = 0,$$
$$q = 0,\ \mathrm{A} = WO_3,\ \mathrm{B} = H_2,\ \mathrm{C} = 0,\ \mathrm{D} = 0,\ \mathrm{E} = WO_{2.9},$$
$$\mathrm{F} = H_2O,\ \mathrm{G} = 0,\ \mathrm{H} = 0$$

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

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

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 [7,8]

$$\Delta_r G^0 = \Delta_f H^0_{298} + \int_{298}^{T} \Delta C_p \,\mathrm{d}T - T\Delta_r S^0_{298} - T\int_{298}^{T} \frac{\Delta C_p}{T}\,\mathrm{d}T \tag{7}$$

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 298 K in the reaction, respectively; T is the temperature in Kelvin; ΔC_p is the changes 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 [7,8]:

$$C_P = a + bT + cT^{-2} + dT^3 + eT^2 \tag{8}$$

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

According to Reaction (5) and Eq. (6), the calculation model is constructed as following:

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

$$\begin{aligned}\Delta_r S^0_{298} = {} & uS^0_{298}(\mathrm{E}) + vS^0_{298}(\mathrm{F}) + pS^0_{298}(\mathrm{G}) + qS^0_{298}(\mathrm{H}) \\ & - xS^0_{298}(\mathrm{A}) - yS^0_{298}(\mathrm{B}) - zS^0_{298}(\mathrm{C}) - wS^0_{298}(\mathrm{D})\end{aligned} \tag{10}$$

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.

$$\begin{aligned}\Delta C_p = {} & uC_p(\mathrm{E}) + vC_p(\mathrm{F}) + pC_p(\mathrm{G}) + qC_p(\mathrm{H}) \\ & - xC_p(\mathrm{A}) - yC_p(\mathrm{B}) - zC_p(\mathrm{C}) - wC_p(\mathrm{D}) \\ = {} & u(a(\mathrm{E}) + b(\mathrm{E})T + c(\mathrm{E})T^{-2} + d(\mathrm{E})T^3 \\ & + e(\mathrm{E})T^2) + v(a(\mathrm{F}) + b(\mathrm{F})T + c(\mathrm{F})T^{-2} \\ & + d(\mathrm{F})T^3 + e(\mathrm{F})T^2) + p(a(\mathrm{G}) + b(\mathrm{G})T \\ & + c(\mathrm{G})T^{-2} + d(\mathrm{G})T^3 + e(\mathrm{G})T^2) + q(a(\mathrm{H}) \\ & + b(\mathrm{H})T + c(\mathrm{H})T^{-2} + d(\mathrm{H})T^3 + e(\mathrm{H})T^2) \\ & - x(a(\mathrm{A}) + b(\mathrm{A})T + c(\mathrm{A})T^{-2} + d(\mathrm{A})T^3 \\ & + e(\mathrm{A})T^2) - y(a(\mathrm{B}) + b(\mathrm{B})T + c(\mathrm{B})T^{-2} \\ & + d(\mathrm{B})T^3 + e(\mathrm{B})T^2) - z(a(\mathrm{C}) + b(\mathrm{C})T \\ & + c(\mathrm{C})T^{-2} + d(\mathrm{C})T^3 + e(\mathrm{C})T^2) - w(a(\mathrm{D}) \\ & + b(\mathrm{D})T + c(\mathrm{D})T^{-2} + d(\mathrm{D})T^3 + e(\mathrm{D})T^2)\end{aligned} \tag{11}$$

where each letter and sign are corresponding with the substances or coefficients in the above reactions and equations, respectively.

According to the Gibbs equation as following:

$$\Delta_r G = \Delta_r G^0 + RT\ \ln K^0 \tag{12}$$

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

$$\begin{aligned}&\Delta_r G^0 = -RT\ln K^0 \ \text{or} \\ &\Delta_r G^0 = -2.303RT\lg K^0\end{aligned} \tag{13}$$

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