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Gibbs free energy of formation of rhodium sulfides

K.T. Jacob [*], Preeti Gupta

Department of Materials Engineering, Indian Institute of Science, Bangalore 560012, India

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ABSTRACT

Using a solid-state electrochemical technique, thermodynamic properties of three sulfide phases ($RhS_{0.882}$, Rh_3S_4, Rh_2S_3) in the binary system (Rh + S) are measured as a function of temperature over the range from (925 to 1275) K. Single crystal CaF_2 is used as the electrolyte. The auxiliary electrode consisting of ($CaS + CaF_2$) is designed in such a way that the sulfur chemical potential converts into an equivalent fluorine potential at each electrode. The sulfur potentials at the measuring electrodes are established by the mixtures of ($Rh + RhS_{0.882}$), ($RhS_{0.882} + Rh_3S_4$) and ($Rh_3S_4 + Rh_2S_3$) respectively. A gas mixture ($H_2 + H_2S + Ar$) of known composition fixes the sulfur potential at the reference electrode. A novel cell design with physical separation of rhodium sulfides in the measuring electrode from CaS in the auxiliary electrode is used to prevent interaction between the two sulfide phases. They equilibrate only via the gas phase in a hermetically sealed reference enclosure. Standard Gibbs energy changes for the following reactions are calculated from the electromotive force of three cells:

$$2.2667Rh\ (s) + S_2\ (g) \rightarrow 2.2667RhS_{0.882}\ (s),$$

$$\Delta_r G^o \pm 2330/(J \cdot mol^{-1}) = -288690 + 146.18\ (T/K),$$

$$4.44RhS_{0.882}\ (s) + S_2\ (g) \rightarrow 1.48Rh_3S_4\ (s),$$

$$\Delta_r G^o \pm 2245/(J \cdot mol^{-1}) = -245596 + 164.31\ (T/K),$$

$$4Rh_3S_4\ (s) + S_2\ (g) \rightarrow 6Rh_2S_3\ (s),$$

$$\Delta_r G^o \pm 2490/(J \cdot mol^{-1}) = -230957 + 160.03\ (T/K).$$

Standard entropy and enthalpy of formation of rhodium sulfides from elements in their normal standard states at $T = 298.15$ K are evaluated.

1. Introduction

Processing ore concentrates containing platinum group metals (PGM) involves smelting to produce a (Fe + Co + Ni + Cu) matte that acts as PGM collector [1]. Hence, accurate information of precious metal–sulfur systems is useful for optimizing PGM recovery. In recent years Rh_xS_y, a balanced mixture of ($Rh_2S_3 + Rh_3S_4 + Rh_{17}S_{15}$) with Rh_3S_4 as an active phase, has emerged as a promising electro-catalyst for the reduction of molecular oxygen to water in acidic medium [2–8]. It is the only commercial chalcogenide electro-catalyst available for oxygen reduction reaction (ORR) applications, such as depolarized electrolysis of HCl. The catalyst has potential applications in fuel cells, especially direct methanol fuel cells (DFMCs). Accurate thermodynamic data for rhodium sulfides will enable better characterization of the electrochemical processes.

In the (Rh + S) binary system, four solid phases, $Rh_{17}S_{15}$ ($RhS_{0.882}$), Rh_3S_4, Rh_2S_3 and $RhS_{\sim 3}$ are reported [9], but the phase diagram is incomplete. The diagram in the compilation of Massalski *et al.* [9] indicates the decomposition of $Rh_{17}S_{15}$ to a Rh–rich liquid sulfide (matte) and sulfur–rich gas at $T \sim 1373$ K. Taylor [10] measured the liquidus and phase transformation temperatures of 11 samples covering the composition range from (45 to 67) atom percent Rh by employing differential thermal analysis (DTA). Contrary to the earlier phase diagram [9], the results of Taylor [10] show the existence of three-phase equilibrium consisting of $Rh_{17}S_{15,}$ Rh_3S_4 and (Rh + S) liquid solution at $T = 1386$ K. Rh_3S_4 decomposes at $T = 1403$ K to form Rh_2S_3 and (Rh + S) liquid. The decomposition temperature of Rh_2S_3 was not determined.

Crystallographic studies on $Rh_{17}S_{15}$ ($RhS_{0.882}$) were reported by Geller [11,12]. $Rh_{17}S_{15}$ is iso-structural with $Pd_{17}Se_{15}$ and has cubic structure with space group *Pm*3*m* and two formula units per unit

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* Corresponding author. Tel.: +91 80 2293 2494; fax: +91 80 2360 0472.
E-mail addresses: katob@materials.iisc.ernet.in, ktjacob@hotmail.com (K.T. Jacob).

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cell [11,12]. $Rh_{17}S_{15}$ is a naturally occurring mineral known as miassite and was first synthesized by Matthias *et al.* [13]. Naren *et al.* [14] have confirmed crystallographic data for $Rh_{17}S_{15}$ and found superconductivity below $T = 5.4$ K caused by the presence of high density of states of Rh d bands near Fermi level. The second sulfide, Rh_3S_4, commonly known as kingstonite, crystallizes with monoclinic structure in the space group C2/*m* [15]. Rh_2S_3, often referred to bowieite, has orthorhombic crystal structure with space group P*bcn* [16].

The Gibbs energy of formation of rhodium sulfides above $T = 1084$ K has been measured using different techniques [10,17,18]. Taylor [10] used the Knudsen effusion technique for measuring the sulfur pressures within the temperature range from (1213 to 1363) K. Larson and Elliott [17] employed a solid-state cell with stabilized-zirconia as the electrolyte, pure oxygen as the reference electrode and mixture of Rh and Rh_xS under 101.3 kPa pressure of SO_2 gas as the measuring electrode in the temperature range from (1084 to 1357) K. They were unable to identify the sulfide phase in equilibrium with Rh. According to the phase diagram suggested by Taylor [10], metallic Rh coexists with liquid (Rh + S) solution (matte) above $T = 1213$ K. There is a significant difference in the temperature dependence of the Gibbs energy of formation of the metal saturated phase, $Rh_{17}S_{15}$ ($RhS_{0.882}$) reported by Taylor [10] and Rh_xS reported by Larson and Elliott [17]. Juza *et al.* [18] used the manometric technique to measure the dissociation pressure two rhodium sulfides (Rh_3S_4 and Rh_2S_3) within the temperature range from (1226 to 1356) K. A solid-state electrochemical cell based on single crystal CaF_2 as the electrolyte is used in this study to extend the measurements to lower temperature so that thermodynamic properties are better defined.

2. Experimental procedure

2.1. Materials

Purity and sources of the chemicals used in this study are given in table 1. Optical grade single crystals of CaF_2 in the form of disks of 1.5 cm in diameter and 0.2 cm thick, were obtained from Harshaw Chemical Company. A high-purity gas mixture of (H_2 + H_2S + Ar) of constant composition containing 0.8 volume fraction Ar, 0.16654 volume fraction hydrogen and 0.03346 volume fraction H_2S supplied by Matheson is used to define the sulfur partial pressure at the reference electrode. The high concentration of Ar in the gas mixture minimizes thermal segregation in the gas mixture caused by the large difference in the atomic mass of the constituents H_2 and H_2S.

Three rhodium sulfides $Rh_{17}S_{15}$ ($RhS_{0.882}$), Rh_3S_4 and Rh_2S_3 are prepared by direct reaction between Rh and S in evacuated and sealed silica ampoules at high temperatures. Rh powder is first reduced under H_2 gas at $T = 873$ K to remove surface oxide. Powders of Rh and S are mixed in the appropriate stoichiometric ratio and sealed in evacuated ampoules. The mixture is reacted initially at $T = 673$ K for 48 h. Temperature is then raised slowly. The final reaction temperatures are $T = 1200$ K for $Rh_{17}S_{15}$ ($RhS_{0.882}$) and $T = 1373$ K for Rh_3S_4 and Rh_2S_3. After holding at the highest temperature for 72 h, the ampoules are furnace cooled. Sulfur condensation on the ampoule indicates incomplete reaction. In such cases, additional heat treatment was done till all the sulfur is consumed. Formation of single phase sulfides is confirmed by X-ray diffraction (XRD) and their composition verified by energy dispersive spectroscopy (EDS). The lattice parameters of the synthesized compounds are $a = 0.9913$ nm for $Rh_{17}S_{15}$, $a = 1.031$ nm, $b = 1.069$ nm, $c = 0.6210$ nm for Rh_3S_4 and $a = 0.8464$ nm, $b = 0.5987$ nm, $c = 0.6141$ nm for Rh_2S_3.

TABLE 1
Sources and purity of chemicals used in the experiment.

Chemicals	Sources	Mass fraction purity
Rh (powder)	Alfa aesar	0.9995
CaF_2 (single crystal)	Harshaw chemicals	0.9999
CaF_2 (powder)	Apache chemical company	0.99999
CaS	Ventron corporation	0.9999
Au wire	Johnson matthey and mallory ltd.	0.999
(H_2 + H_2S + Ar) gas mixture	Matheson	0.99999
S (powder)	Alfa aesar	0.995

2.2. Electrochemical measurements

The electromotive force (e.m.f.) of the following solid-state electrochemical cells were measured,

$$\text{Au,}H_2 + H_2S/CaS + CaF_2//CaF_2//CaF_2 + CaS/Rh + RhS_{0.882}, \text{Au}\ , \tag{I}$$

$$\text{Au,}H_2 + H_2S/CaS + CaF_2//CaF_2//CaF_2 + CaS/RhS_{0.882} + Rh_3S_4,\ \text{Au}, \tag{II}$$

$$\text{Au,}H_2 + H_2S/\ CaS + CaF_2//CaF_2//\ CaF_2 + CaS/Rh_3S_4 + Rh_2S_3, \text{Au}. \tag{III}$$

Single crystal CaF_2 used as the solid electrolyte is an F^- ion conductor and responds to the difference in the chemical potential of fluorine at the two electrodes. At each electrode, ($CaS + CaF_2$) pellet is used to convert the sulphur chemical potential into an equivalent fluorine potential [19] by virtue of the exchange reaction;

$$CaF_2 + 1/2S_2 \rightarrow CaS + F_2. \tag{1}$$

There is negligible solid solubility between CaF_2 and CaS and both phases are present at unit activity at the auxiliary electrodes. The cell e.m.f. is thus related to the difference in the sulfur chemical potential established at the electrodes.

Several examples of the use of auxiliary electrodes are reported in the literature. Auxiliary electrode of CaS has been used to convert sulfur chemical to an equivalent oxygen potential in conjunction with CaO-stabilized ZrO_2 [20]. An auxiliary electrode of Na_2S has been used for sulfur potential measurement along with Na β-alumina, which is a Na^+ ion conductor [21]. Na_2SO_4 has been used as an auxiliary electrode in probes for SO_2/SO_3 based on Na β-alumina [22]. Similarly, a ($CaSO_4 + CaF_2$) auxiliary electrode has been used to measure the partial pressure of SO_3 using a solid-state cell based on CaF_2 as electrolyte [23].

The gas reference electrode on the left-hand side of each cell is connected to the negative terminal of a high impedance ($>10^{12}$) digital voltmeter. The ($H_2 + H_2S$ + Ar) gas mixture establishes the sulfur potential at the reference electrode. A mixture of two adjacent phases in the (Rh + S) system fixes the sulfur potential at the measuring electrodes. When the sulfur chemical potential of the measuring electrode is higher than that of the reference, the cell e.m.f. is positive. The e.m.f. values for cell (I) is measured in the range temperature from (925 to 1200) K, cell (II) and cell (III) from (925 to 1275) K. The upper temperature limit for cell (I) is set by the formation of eutectic liquid at $T = 1213$ K [11]. The upper limit for cells (II) and (III) is set by the softening of CaF_2 single crystal, which serves as an electrolyte.

A schematic outline of apparatus used for e.m.f. measurement is displayed in figure 1. Auxiliary electrode pellets composed of ($CaS + CaF_2$) are spring-loaded on both sides of single crystal CaF_2