Formation Gibbs Energy of Na_2RuO_3 ⁺

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ABSTRACT

By employing a thermogravimetric technique, the standard Gibbs energy changes for reaction

were determined to be

$$\Delta G^\circ(l)/\text{J mol}^{-1} = (362,000 \pm 20,000) - (297 \pm 18)(T/\text{K})$$

between 1123 and 1203K.

INTRODUCTION

Spent fuel generated from nuclear power stations normally contains ruthenium dioxide, RuO_2 . When nuclear waste was melted together with boro-silicate glasses in glass melting furnace, in order to immobilize radioactive elements, ruthenium dioxide would often exist as a separate solid phase. This is due to very small solubilities of ruthenium dioxide in the glasses. The heating of glasses relies on the passage of electrical current through glass melts. Since ruthenium dioxide has relatively high electrical conductivities /1/, the

presence of solid ruthenium dioxide causes non-uniform current- and temperature-distributions within the glass melts. Such non-uniformity of temperature results in partly solidified glasses, which eventually would plug tapping nozzle of the furnace. X-ray diffraction analysis made on glasses that caused nozzle clogging revealed the presence of ruthenium dioxide as a separate phase. A potential solution to remove such solidified glass would be the addition of sodium carbonate. The authors expected that, at temperatures greater than the melting point, sodium carbonate would dissolve ruthenium dioxide to form homogeneous fluid. However, in practice, such dissolution of ruthenium dioxide was not observed. It was felt that liquid Na_2CO_3 would react with solid RuO_2 to form solid Na_2RuO_3 , rather than diluting RuO_2 :

$$\Delta G^\circ(l) = -RT \ln P_{\text{CO}_2} \quad (2)$$

In equation (1) and hereafter Kubaschewski-Alcock notation /2/ is used. Shaplygin and Lazarev /3/ have reported the formation of Na_2RuO_3 through reaction (1) at ambient atmosphere. Based on this background, it became necessary to know the standard Gibbs energy changes for reaction (1), which have not been reported

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Fig. 1: Pressure – temperature diagram for the system Ru–O. Open circles indicate the oxygen partial pressures and temperature used in this experiment.

in the literature. The present study is aimed at determining the $\Delta G^\circ(I)$ values by employing a thermogravimetric technique.

With respect to stability of ruthenium dioxide, a few words seem to be pertinent. Figure 1 shows the pressure-temperature diagram of the system Ru–O. At the temperature range given in this diagram, RuO_3 occurs at gaseous state, while Ru and RuO_2 exist at solid state. Hence the stability field for RuO_2 depend upon the partial pressures of RuO_3 . The phase boundary expressed by dotted lines correspond to $P_{\text{RuO}_3} = 10^{-6}$ atm.

EXPERIMENTAL ASPECTS

Figure 2 shows the experimental apparatus, which consisted of a thermobalance, gas purification train, a SiC resistance furnace, an oxygen sensor and a gas mixer. The details of the thermobalance have been reported elsewhere [4]. The thermobalance allowed continuous weight measurements with an accuracy of ± 0.1 mg. The gas purification train consisted of silica gel and phosphorous pentoxide. In order to minimize the fluctuations in the gas flow rate, the gas was

admitted to the mullite reaction tube through 1-mm i.d. capillary tube. The SiC resistance furnace was equipped with a mullite reaction tube of 30-mm o.d., 24-mm i.d. and 600-mm long. An oxygen sensor was equipped within gas purification train in order to ensure that oxygen partial pressures would be low enough to avoid or at least minimize vaporization of ruthenium as RuO_3 . The details of oxygen sensor incorporating zirconia solid electrolyte have been reported elsewhere [5].

First, preliminary experiments were conducted to confirm the formation of Na_2RuO_3 at $P_{\text{CO}_2} = 0$, in conforming to reaction [1]. An equimolar mixture of Na_2CO_3 (49.5 mg) and RuO_2 (62.2 mg) was compacted to a pellet of 10-mm diameter and 1-mm thickness. This mixture, contained in a platinum crucible of 17-mm i.d. and 13-mm height, was suspended via a platinum chain and heated to 1173 K under a stream of argon. By using the oxygen sensor, the oxygen partial pressure in argon was determined to be $10^{-4.3}$ atm. At 1173K, weight decrease of 21.3 mg was observed. This value of 21.3 mg should be compared with the theoretical value of 20.6 mg; $(49.5 \text{ mg}) \times (44.01/105.99) = 20.6 \text{ mg}$. The reaction product was subsequently submitted to X-ray diffraction analysis. Table 1 gives the diffraction

Fig. 2: Experimental apparatus.

Table 1
Diffraction indexes of Na_2RuO_3 with Cu- α

2 θ (degree)	Intensity	2 θ (degree)	Intensity
16.561	100	62.148	6
33.363	31	67.963	9
33.661	40	69.372	11
34.778	41	69.985	13
35.120	32	70.880	7
35.580	3	73.420	9
40.051	100	74.083	7
40.340	83	75.633	4
43.786	10	76.860	5
52.309	21	77.223	17
57.198	39	77.620	15
58.671	17	77.960	12
59.389	11	78.509	11
60.160	5	79.000	10
60.460	6	79.360	8
61.446	7	79.800	8

indexes of the resulting compounds, Na_2RuO_3 , obtained in this study. The X-ray indices reported by Shaplygin and Lazarev /3/ are for samples prepared through

mixing Na_2O_2 and RuO_2 under an ambient atmosphere, at which RuO_2 is not stable.

Thermogravimetric measurements for Gibbs energy determinations were conducted by heating equimolar mixture of $\text{Na}_2\text{CO}_3 + \text{RuO}_2$ to the experimental temperatures in a stream of pure CO_2 at a flow rate of 300 cc/min. By adjusting the Ar/ CO_2 mixing ratio on the gas mixer, the partial pressure of CO_2 was then lowered gradually. The CO_2 partial pressures were further decreased until weight decrease was observed. A representative recorder chart obtained through such measurements is given in Figure 3. As shown in this figure weight decreases was observed upon P_{CO_2} was changed to 0.040 atm from 0.051 atm. In this way, gravimetric measurements were repeated at temperatures between 1123 and 1203 K. As can be seen from Figure 1, because of instability of RuO_2 , experiments were restricted to temperatures below 1203 K. At $T < 1123$ K, reaction rate was too slow to be detected *via* thermogravimetric measurements, since the reaction is solid/solid reaction, rather than between liquid and solid phases. It is noted here that the melting point of Na_2CO_3 is 1123K /6/. Open circles in Figure 1 indicate P_{O_2} and T used for experiments. By using the values for P_{O_2} and T given in this figure, the partial

Fig. 3: Representative recorder chart obtained via thermogravimetric measurements.

pressures of RuO_3 were estimated to be less than $10^{-6.9}$ atm.

EXPERIMENTAL RESULTS AND DISCUSSIONS

In Figure 4, solid and open circles correspond to weight decrease and no-weight changes, respectively. The straight line drawn in Figure 4 corresponds to an expression with the correlation factor, r^2 , of 0.907:

$$\log \{P_{\text{CO}_2} / \text{atm}\} = (-18,890 \pm 1070) / (T/\text{K}) + (15.53 \pm 0.92) \quad (3)$$

It follows that

$$\Delta G''(l) / \text{J mol}^{-1} = -RT \ln P_{\text{CO}_2} = (362,000 \pm 20,000) - (297 \pm 18) (T/\text{K}) \quad (4)$$

This positive value of $297 \pm 18 \text{ J mol}^{-1} \text{ K}^{-1}$ for the second-law entropy would be acceptable, since through reaction [1], one gas molecule is formed from two condensed phases [7]. In Figure 4, the equilibrium CO_2 partial pressures of reaction [1] are compared with those for the decomposition of Na_2CO_3 [8].

Fig. 4: Relation between $\log P_{\text{CO}_2}$ and $1/T$.

For example, at 1250 K and in the absence of RuO_2 , Na_2CO_3 is stable so far as CO_2 partial pressures are greater than $10^{-6.17}$ atm. In the presence of RuO_2 , in order to stabilize Na_2CO_3 , however, CO_2 partial pressures have to be greater than $10^{0.418}$ atm. In this context, it is mentioned that the CO_2 partial pressure of ambient atmosphere is 3×10^{-8} atm /9/. Hence, in the presence of RuO_2 , reaction (1) proceeds to the right-hand side at ambient atmosphere.

CONCLUSION

For better understanding of the glass immobilization process for nuclear waste, the standard Gibbs energy changes for the formation of $\langle \text{Na}_2\text{RuO}_3 \rangle$ were determined to be

$$\Delta G^\circ(l)/\text{J mol}^{-1} = (362,000 \pm 20,000) - (297 \pm 18)(T/\text{K})$$

between 1123 and 1203K.

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