# STANDARD GIBBS ENERGIES OF FORMATION OF RuO<sub>2</sub>(s) AND LaRuO<sub>3</sub>(s) BY OXIDE e.m.f. MEASUREMENTS

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## Summary

The e.m.f. of the galvanic cells

Pt, Ru, 
$$RuO_2|15$$
 YSZ $|O_2(P_{O_2} = 0.21 \text{ atm})$ , Pt (1)

and

$$Pt, Cu, Cu_2O|8 YSZ|RuO_2, Ru, Pt$$
(II)

(YSZ is  $Y_2O_3$ -stabilized ZrO<sub>2</sub>) were measured over the ranges 1005-1106 K and 751-1200 K respectively, yielding the least-squares expressions

$$E_{(1)} = 813.57 - 0.50242T \pm 2.52 \text{ mV}$$
<sup>(1)</sup>

and

$$E_{\rm (II)} = 80.27 + 0.07035 \, T \pm 1.33 \, \mathrm{mV} \tag{2}$$

From these results, the standard Gibbs energy of formation of  $\text{RuO}_2$  was determined to be

$$\Delta G_{\rm f}^{\circ} ({\rm RuO}_2({\rm s})) = -305464 + 172.70 \, T \pm 1245 \, {\rm J} \, {\rm mol}^{-1} \tag{3}$$

A third-law analysis yielded a value of  $-313.9\pm0.7$  kJ mol<sup>-1</sup> for  $\Delta H_{\rm f}^{\circ}$  (RuO<sub>2</sub>(s), 298.15 K). A partial phase diagram of the La-Ru-O system was determined, based on which the e.m.f. of the cell

Pt, LaRuO<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, Ru|15 YSZ|O<sub>2</sub> (
$$P_{O_2} = 0.21$$
 atm), Pt (III)

was measured over the range 1032-1256 K yielding the expression

$$E_{\text{(III)}} = 844.14 - 0.49906 \, T \pm 2.40 \, \text{mV} \tag{4}$$

From this  $\Delta G_{\rm f}^{\circ}$  (LaRuO<sub>3</sub>(s)) = -1175350 + 274.57 T J mol<sup>-1</sup> was derived. The consistency of  $\Delta G_{\rm f}^{\circ}$  (LaRuO<sub>3</sub>(s)) was verified by e.m.f. measurements on the cell

$$Pt, Cu, Cu_2O|8 YSZ|LaRuO_3, RuO_2, La_2O_3, Pt$$
(IV)

at two temperatures.

# 1. Introduction

The oxide  $RuO_2$  is of interest to solid state scientists in view of its remarkable electrical, optical, magnetic and catalytic properties [1-3]. The perovskite-type ternary oxide LaRuO<sub>3</sub> is well known as a catalyst and promoter in the chemical industry [4]. In addition, the compounds of lanthanum and ruthenium are of importance to fast nuclear reactor technology in understanding the chemical state of fission products in the spent nuclear fuels [5, 6]. Recently, Cordfunke et al. [7] have exhaustively reviewed all the thermochemical properties of  $RuO_2(s)$  based on their own calorimetric and e.m.f. measurements, as well as assessing earlier reports wherein these two techniques were employed [1, 8-13]. Earlier, Kleykamp [10]also assessed the thermochemical data on RuO<sub>2</sub>, obtained mainly from vapour pressure measurements reported in the literature, while discussing his e.m.f. results. The rather large scatter even amongst the results reported by Kleykamp [10], Pizzini and Rossi [11], Chatterii and Vest [12] and Cordfunke and Konings [1], employing the same oxide e.m.f. technique, has prompted this redetermination of  $\Delta G_{\rm f}^{\circ}$  of RuO<sub>2</sub>(s). Further, practically no information is available in the literature on the experimental values of  $\Delta G_{f}^{\circ}$  of LaRuO<sub>3</sub>(s). Hence, this paper also presents the results on  $\Delta G_{\rm f}^{\circ}$  of LaRuO<sub>3</sub>(s) based on the e.m.f. technique after ascertaining the phases coexisting with this compound by equilibrium studies.

# 2. Experimental details

RuO<sub>2</sub> (Johnson-Matthey Chemicals, U.K.), La<sub>2</sub>O<sub>3</sub> (Indian Rare Earths Ltd.), electrolytic copper (Spex Industries, Inc., U.S.A.) and CuO (E. Merck), all of which had a purity better than 99.9%, were used as the starting substances. The oxide RuO<sub>2</sub> was reduced in hydrogen at 873 K for 2 h to produce reactive ruthenium powder. Equimolar mixtures of La<sub>2</sub>O<sub>3</sub>, RuO<sub>2</sub> and ruthenium were compacted into cylindrical pellets of diameter 10 mm and thickness 3-4 mm at a pressure of 100 MPa. These pellets were heated in air at 1273 K for 24 h. This procedure of grinding, compacting and heating was repeated at least three times, followed by final heating in air at 1473 K and 1673 K for 8 h and 4 h respectively. The product was found to be pure LaRuO<sub>3</sub>(s) within the 5 wt.% limits of detection of impurity phases by powder X-ray diffractometry.

Phase equilibrium studies were made on pellets prepared by a similar procedure from mixtures of LaRuO<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, RuO<sub>2</sub> and ruthenium, taking three phases at a time and heating in a stream of argon at 1273 K for 24 h prior to examination by XRD. One set of test electrodes used in e.m.f. studies was made from the equimolar mixture of the coexisting phases LaRuO<sub>3</sub>, ruthenium and La<sub>2</sub>O<sub>3</sub> by compacting into pellets of diameter 10 mm and thickness 2 mm at a pressure of 100 MPa. The second set of test electrodes was similarly prepared from an equimolar mixture of the coexisting phases LaRuO<sub>3</sub>, RuO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub>. The third set was made of ruthenium and RuO<sub>2</sub> in the mass ratio of 4:1. The Cu/Cu<sub>2</sub>O reference electrodes were made from a 4:1 (mass ratio) mixture of copper and Cu<sub>2</sub>O, the latter being produced by heating powdered CuO in a stream of purified argon (oxygen content less than 10 ppm) at 1273 K for 4 h. Two types of electrolytes were used in the e.m.f. measurements described below. For the two compartment cell, cylindrical solid electrolyte tubes with one end closed and closed end flat having a composition of 15 wt.% Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub> (15 YSZ, Corning, U.S.A.) conforming to the dimensions outer diameter 12.7 mm, inner diameter 9.8 mm and length 300 mm were employed. For the open-cell-stacked pellet assembly, cups made of 8 YSZ with the dimensions outer diameter 10 mm, inner diameter 7 mm and depth 5 mm with a flat bottom (Nippon Kagaku Togyo Co. Ltd.) were employed. Helium gas purified by passing through a trap containing a refrigerated molecular sieve at a very low flow rate (less than 1 dm<sup>3</sup> h<sup>-1</sup>) provided the inert gas blanket wherever required in both the cells. In addition, titanium sponge was employed as an in situ getter of oxygen in the vicinity of the test electrodes. The temperature was measured by a Pt-10%Rh/Pt thermocouple calibrated at the freezing points of high purity tin, zinc, bismuth and silver. A symmetric galvanic cell with identical Fe/"FeO" electrodes sandwiching a disc of YSZ was used to check the absence of asymmetric potentials in the stacked pellet assembly. In the case of two compartment assembly, the e.m.f. of one atmosphere of  $O_2$  against an air electrode was measured both for the purpose of verifying the absence of asymmetric potentials and for correcting for the standard state of oxygen during the computation of the standard Gibbs energy changes for the cell reactions. The same experimental assemblies (including the furnaces) have been employed in many earlier investigations [14–17], obviating the necessity for checking the absence of thermo e.m.f.s etc. Only those cell voltages which did not drift by more than a fraction of a millivolt per hour and which were reproducible during the subsequent heating cycles were taken into account. The other experimental details are described elsewhere [14, 18].

The following galvanic cell arrangements were employed in the present study

Pt, Ru, 
$$RuO_2|15 YSZ|O_2(P_{O_2}=0.21 \text{ atm})$$
, Pt (1)

$$Pt, Cu, Cu_2O|8 YSZ|RuO_2, Ru, Pt$$
(II)

Pt, LaRuO<sub>3</sub>, Ru, La<sub>2</sub>O<sub>3</sub>|15 YSZ|O<sub>2</sub> ( $P_{O_2} = 0.21$  atm), Pt (III)

$$Pt, Cu, Cu_2O|8 YSZ|LaRuO_3, Ru, La_2O_3, Pt$$
(IV)

and

$$Pt, Cu, Cu_2O|8 YSZ|RuO_2, LaRuO_3, La_2O_3, Pt$$
(V)

Where air was used as the reference electrode material (cells (I) and (III)), a twocompartment cell assembly described elsewhere [19] was employed. For cells (II), (IV) and (V), an open-cell-stacked pellet assembly [20] was employed. One important modification with regard to the protection of the platinum lead was made in the e.m.f. measurements with cells (II)–(V) after observing a large scatter in the e.m.f. results from cell (I). This followed the observations by Cordfunke and Konings [1], who attributed the scatter in the values of e.m.f. reported by Pizzini and Rossi [11] and Chatterji and Vest [12] to the possible attack of platinum by ruthenium (owing to 62 at.% solid solubility of ruthenium in platinum as reported by Hutchinson [21]). The precaution taken in cells (II)-(V) was to envelope the ruthenium bearing electrodes in a platinum foil cup in order to minimize the platinum lead-ruthenium interaction.

### 3. Results and discussion

The e.m.f. results of cells (I) and (III) using air as the reference electrode are shown in Fig. 1. Figure 2 shows the e.m.f. results on cell (II). The following least-squares expressions represent the e.m.f. data on cells (I)–(III) over the temperature ranges 1005-1106 K, 751-1200 K and 1032-1256 K respectively

$$E_{(1)} = 813.57 - 0.50242T \pm 2.52 \,\mathrm{mV} \tag{1}$$

(2)

 $E_{\rm (II)} = 80.27 \pm 0.07035 \, T \pm 1.33 \, {\rm mV}$ 



Fig. 1. E.m.f. results of the cells (I) and (III): cell (I): Pt, Ru,  $RuO_2|YSZ|O_2$  ( $P_{O_2}=0.21$  atm), Pt; cell (III): Pt,  $LaRuO_3$ ,  $La_2O_3$ ,  $Ru|YSZ|O_2$  ( $P_{O_2}=0.21$  atm), Pt.



Fig. 2. E.m.f. results of the cell (II); Pt, Cu, Cu<sub>2</sub>O|YSZ|RuO<sub>2</sub>, Ru, Pt.

# and

$$E_{\rm (III)} = 844.14 - 0.49906 \,T \pm 2.40 \,\,\mathrm{mV} \tag{3}$$

To check the internal consistency between cells (I) and (II), the e.m.f. results from both were converted into those for the hypothetical cell

$$Pt, Ru, RuO_2 | YSZ | O_2 (P_{O_2} = 1 \text{ atm}), Pt$$
(VI)

by correcting for the standard state of oxygen in cell (I) and by making use of the precise values of  $\Delta G_{\rm f}^{\circ}$  (Cu<sub>2</sub>O(s)) calculated for each temperature from the data by Charatte and Flengas [22] for cell (II). The e.m.f. values computed in this way for cell (VI) are shown in Fig. 3. It can be seen from Fig. 3 that the consistency in the results between cells (I) and (II) is quite good in spite of not protecting the platinum lead in cell (I) (as was done in the case of cell (II) mentioned earlier). Based on this



Fig. 3. E.m.f. results of the hypothetical cell (VI): Pt, Ru,  $RuO_2|YSZ|O_2$  ( $P_{O_2} = 1$  atm), Pt (computed from the e.m.f. results of cells (I) and (II)).



Fig. 4. Standard Gibbs energy of formation of RuO<sub>2</sub>(s) from e.m.f. measurements.

plot, the following least-squares expression was derived for  $\Delta G_{\rm f}^{\circ}$  (RuO<sub>2</sub>(s)) valid over the range 751–1200 K

$$\Delta G_{\rm f}^{\circ}({\rm RuO}_{\rm 2}({\rm s})) = -305464 + 172.70\,T \pm 1245\,{\rm J\,mol^{-1}} \tag{4}$$

In Fig. 4 expression (4) is compared with those values reported in the recent literature [1, 10–12], all of which were based on solid electrolyte e.m.f. measurements. The present line for  $\Delta G_{\rm f}^{\circ}$  of RuO<sub>2</sub>(s) is in excellent agreement with that found by Cordfunke and Konings [1]. The agreement is fair with data from other investigators.

To assess the temperature-dependent errors in the present c.m.f. results and to compute the standard enthalpy of formation  $\Delta H_{\rm f}^{\circ}$  (RuO<sub>2</sub>(s), 298.15 K), it is customary to perform a third-law analysis. For this purpose, reliable calorimetric data on Ru(s) and RuO<sub>2</sub>(s) were needed. A comparison of the thermochemical data from the recent compilations [23, 24] with those cited by Kleykamp [10] and Cordfunke *et al.* [7] reveals that there are considerable discrepancies in the values of the free energy functions  $\Phi$  from one set to another. It is found that the tabulation of  $\Phi$  values by Cordfunke *et al.* [7] was based on their careful adiabatic and drop calorimetric measurements, and hence these values were adopted for the third-law treatment. Since it was necessary to extrapolate the values of  $\Phi$  cited by

## TABLE 1

Values of free-energy functions used for computing  $\Delta H_{f}^{\circ}(\text{RuO}_{2}(s), 298.15 \text{ K})$ 

Element/compound	Free-energy function $(J K^{-1} mol^{-1})$			Reference
	800 K	1000 K	1200 K	
Ru(s)	- 37.69	- 41.65	-45.46ª	25
$O_2(g)$	-216.13	-220.88	-225.21	26
$RuO_2(s)$	-69.89	-81.08	- 92.18 <sup>b</sup>	7

<sup>a</sup>Extrapolated from ref. 25.

<sup>b</sup>Extrapolated from ref. 7.



Fig. 5.  $\Delta H_{f}^{\circ}(\text{RuO}_{2}(s), 298.15 \text{ K})$  determined by third-law computations from the Gibbs energy data.

Cordfunke and Konings [25] and Cordfunke *et al.* [7] beyond 1000 K for ruthenium and RuO<sub>2</sub> respectively the actual values used here are listed in Table 1 along with those for oxygen from recent JANAF thermochemical tables [26]. Combining the values in Table 1 with the data points in Fig. 3, values of  $\Delta H_{\rm f}^{\circ}$  (RuO<sub>2</sub>(s), 298.15 K) were computed by third-law analysis and are plotted against the temperature of measurement in Fig. 5. A mean value of  $-313.9 \pm 0.7$  kJ mol<sup>-1</sup> was determined for the  $\Delta H_{\rm f}^{\circ}$  (RuO<sub>2</sub>(s)), (298.15 K), agreeing well with the value of  $-314.15 \pm 0.02$  kJ mol<sup>-1</sup> obtained by Cordfunke *et al.* [7] and with other values in the range -312.5 to -317.8 recalculated by Cordfunke and Konings [1] from the literature [8–13, 27].

In order to determine the standard Gibbs energy of formation of  $LaRuO_3(s)$ by the e.m.f. method, it is necessary to establish the phases coexisting with this compound. As mentioned earlier, phase analyses were carried out using XRD on different three-phase mixtures chosen from La2O3, RuO2, LaRuO3 and ruthenium, after equilibrating the compacted pellets at 1273 K for 24 h under an argon atmosphere. This proved the coexistence of LaRuO<sub>3</sub> with La<sub>2</sub>O<sub>3</sub>/Ru, RuO<sub>2</sub>/Ru and  $La_2O_3/RuO_2$ . Obviously,  $La_2O_3$ ,  $RuO_2$  and ruthenium cannot coexist (see LaRuO<sub>3</sub>) preparation in Section 2). A partial phase diagram determined in this way at 1273 K is shown in Fig. 6. The e.m.f. measurements made on the LaRuO<sub>3</sub>/La<sub>2</sub>O<sub>3</sub>/Ru electrode using the cell (III) are also included in Fig. 1 and the least-squares expression for these results are given in eqn. (3). To check the consistency of these values independently, cell (IV) was constructed and the e.m.f. was measured at a fixed temperature of 985 K, which yielded a value of  $117.3 \pm 2$  mV. This was in good agreement with 113.6 mV computed from eqn. (3) after correcting for the voltage of  $air/O_2$  (1 atm) cell at the same temperature. For reasons not quite clear at present, the stacked pellet assembly was not found to function satisfactorily for the electrode bearing the ternary phase; at temperatures above 1000 K the cell deteriorated very rapidly, whereas below 900 K it did not equilibrate even after holding the temperature constant for 2-3 days. After correcting for the standard



Fig. 6. Phase equilibrium diagram of La-Ru-O system at 1273 K.

state of oxygen in the air reference electrode in cell (III), the standard Gibbs energy change  $\Delta G_r^\circ$  for the passage of 3F of electricity was computed and is given by

$$\Delta G_r^\circ = -244346 + 134.47T \pm 690 \,\mathrm{J} \,\mathrm{mol}^{-1} \tag{5}$$

for the overall cell reaction

$$1/2 \text{La}_2 O_3(s) + \text{Ru}(s) + 3/4 O_2(g) \rightarrow \text{La} \text{Ru} O_3(s)$$
 (6)

Thus

$$\Delta G_{\rm f}^{\circ} \left( {\rm LaRuO}_{\rm 3}({\rm s}) \right) = \Delta G_{\rm r}^{\circ} + 1/2 \,\Delta G_{\rm f}^{\circ} \left( {\rm La}_{\rm 2} {\rm O}_{\rm 3}({\rm s}) \right) \tag{7}$$

Using the expression

$$\Delta G_{\rm f}^{\circ}({\rm La}_{2}{\rm O}_{3}({\rm s})) = -1862000 + 280.2T \,{\rm J}\,{\rm mol}^{-1} \tag{8}$$

derived from the thermochemical tables [28] for the suitable temperature range,  $\Delta G_{f}^{\circ}(\text{LaRuO}_{3}(s))$  was found to be

$$\Delta G_{\rm f}^{\circ} (\text{LaRuO}_{3}(s)) = -1175350 + 274.57 \, \text{J} \, \text{mol}^{-1} \tag{9}$$

Equation (9) is valid over the temperature range 1032–1256 K. The uncertainty in the value of  $\Delta G_{\rm f}^{\circ}({\rm La}_2{\rm O}_3({\rm s}))$  is of the order of 16.7 kJ mol<sup>-1</sup> which, when taken into consideration, would give rise to  $\pm 9$  kJ mol<sup>-1</sup> for the standard deviation in the value of  $\Delta G_{\rm f}^{\circ}({\rm LaRuO}_3({\rm s}))$ .

In order to determine  $\Delta G_{\rm f}^{\circ}$  (LaRuO<sub>3</sub>(s)) from an independent measurement, cell (V) was constructed and the e.m.f. was measured to be 264.7 mV and 261.7 mV at 942.5 K and 956.4 K respectively. These temperatures of around 950 K for e.m.f. measurements were chosen for reasons stated earlier. On the basis of the reaction

$$Cu(s) + RuO_2(s) + 1/2 La_2O_3(s) \rightarrow LaRuO_3(s) + 1/2 Cu_2O(s)$$
 (10)

 $\Delta G_{f}^{\circ}$  (LaRuO<sub>3</sub>) was calculated for the passage of 1 F of electricity. Incorporating the values of  $\Delta G_{f}^{\circ}$  of Cu<sub>2</sub>O(s), La<sub>2</sub>O<sub>3</sub>(s) and RuO<sub>2</sub>(s) at 942.5 and 956.4 K, the values of -917.4 kJ mol<sup>-1</sup> at 942.5 K and -913.3 kJ mol<sup>-1</sup> at 956.4 K were computed from the two e.m.f. values for cell (V). These are in good agreement with -916.6 and -912.8 kJ mol<sup>-1</sup> calculated from eqn. (9) from cell (III). Combining eqns. (4), (8) and (9),  $\Delta G_{r}^{\circ}$  for the phase equilibrium

$$LaRuO_{3}(s) + 1/4 O_{2}(g) \rightarrow 1/2 La_{2}O_{3}(s) + RuO_{2}(s)$$
 (11)

was calculated to be

$$\Delta G_{\rm r}^{\circ}(11) = -61114 + 38.23 \, T \, \mathrm{J} \, \mathrm{mol}^{-1} \tag{12}$$

The log  $P_{O_2}$  values derived from eqns. (4), (9) and (12) for the buffer mixtures Ru/RuO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>/LaRuO<sub>3</sub>/Ru and La<sub>2</sub>O<sub>3</sub>/RuO<sub>2</sub>/LaRuO<sub>3</sub> at two interpolated temperatures (1000 and 1200 K) from the present work are given in Table 2. From Table 2 it can be seen that the equilibrium oxygen pressure over La<sub>2</sub>O<sub>3</sub>/Ru/LaRuO<sub>3</sub> is only marginally lower than that for Ru/RuO<sub>2</sub>, thereby explaining the difficulties experienced in the synthesis of the perovskite. There are no reliable measurements

### TABLE 2

 $log P_{O_{\gamma}}(atm) = A - B/T (K)$ **Buffer mixture**  $log P_{O_2}(atm)$ 1000 K 1200 K -6.94Ru/RuO, 9.022 - 15957/T-4.289.366 - 17019/T $La_2O_3/Ru/LaRuO_3$ -7.65 -4.827.988 - 12770/T-4.78 -2.65 La<sub>2</sub>O<sub>3</sub>/RuO<sub>2</sub>/LaRuO<sub>3</sub>

Comparison of equilibrium dissociation pressures of  $RuO_2(s)$  and  $LaRuO_3(s)$ 

available in the published literature to allow us to compare the values of  $\Delta G_{\rm f}^{\circ}$  of LaRuO<sub>3</sub>(s); a third-law assessment is even more difficult. However, the slope of  $\Delta G_{\rm f}^{\circ}$  (LaRuO<sub>3</sub>) appears to be as reasonable as could be expected for the loss of translational entropy associated with 0.75 mol of oxygen gas.

Earlier, a systematic decrease in  $\Delta G_{\rm f}^{\circ}$  of LaMO<sub>3</sub> (M = Mn, Fe, Co, Ni or Cu) was reported by Sreedharan *et al.* [29] from similar e.m.f. measurements. In the case of LaM'O<sub>3</sub> compounds, where M' is a corresponding element in the 4d transition series, no such comparison is possible owing to the lack of data. However, even lower stability could be predicted for LaM'O<sub>3</sub> than for LaMO<sub>3</sub>. As LaRuO<sub>3</sub> is much less stable than the corresponding LaFeO<sub>3</sub>, falling in between LaNiO<sub>3</sub> and LaCuO<sub>3</sub>, LaRhO<sub>3</sub> should be even less stable and LaPdO<sub>3</sub> is unknown. The lower stability of LaRhO<sub>3</sub> was experienced by the authors in their failure to prepare LaRhO<sub>3</sub> in the pure form by adopting the procedure followed by Wold *et al.* [30].

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