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Thermodynamic stability of $CaRuO_3$

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Abstract

The e.m.f. of the galvanic cell Pt, CaO, $CaRuO_3$, Ru|15 CSZ|O_2 ($P_{O_2}=0.21$ atm), Pt was studied over the range 971–1312 K using 15wt.%CaO-stabilized ZrO_2 (15 CSZ) as the solid electrolyte. This study yielded the least-squares expression $E_{(1)}=754.16-0.36659T\pm1.70$ mV. After correcting for the standard state of oxygen in the air reference electrode and by combining these results with the standard Gibbs energy data on RuO_2 from the literature, the standard Gibbs energy of formation $\Delta G^\circ_{f,\ ox}$ of $CaRuO_3$ from CaO and RuO_2 was determined to be $\Delta G^\circ_{f,\ ox}(CaRuO_3(s))=14396-44.221T\pm1905$ J mol^{-1}.

1. Introduction

The thermodynamic stabilities of ternary oxides with perovskite structure are of considerable interest in solid state chemistry [1–7]. Some reports are available on the magnetic properties of alkaline earth ruthenates [2, 3, 7]. For example, orthorhombic $CaRuO_3$ was reported to be antiferromagnetic while its analogue $SrRuO_3$ was found to be ferromagnetic [2]. Further, $CaRuO_3$-based anodes have been employed in the manufacture of chlorine [4]. The solid solutions $Ca_xSr_{1-x}RuO_3$ were studied by techniques such as Mössbauer spectroscopy for understanding magnetic interactions [6, 8, 9]. It is also known that $CaRuO_3$ is the only stable solid ternary oxide in the CaO–RuO_2 system, whereas the SrO–RuO_2 system is more complicated with the presence of three or four stable ternary phases [10]. However, no reliable information is available on any of the thermochemical properties of the orthorhombic perovskite $CaRuO_3$ in the literature. The thermodynamic data on this compound would serve as a base for comparison of the stabilities of fission-product compounds $SrRuO_3$ and $BaRuO_3$ as and when they were determined. Hence this study based on the solid oxide electrolyte galvanic cell e.m.f. technique was undertaken to determine the standard Gibbs energy data on $CaRuO_3$.

2. Experimental details

Aragonite ($CaCO_3$) (purity better than 99.5%, E. Merck, India) and $RuCl_3$ (purity greater than 99.9%, Johnson-Matthey Chemicals, U.K.) were used as

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the starting materials. RuO_2 was produced by heating $RuCl_3$ powder in a stream of oxygen at 923 K for 6 h. Reactive ruthenium powder was produced from RuO_2 by reducing the oxide in hydrogen at 873 K for 3 h. An equimolar mixture of $CaCO_3$ and ruthenium was blended together and compacted at a pressure of 100 MPa into cylindrical pellets of 10 mm diameter and 2–3 mm thickness. These pellets were subsequently heated in air at 1323 K for 18 h. This procedure of grinding, compacting and heating was repeated twice. The sintered pellets were finally ground, recompacted and heated at 1273 K in air for 24 h to ensure completion of the reaction. The compound was found to be pure $CaRuO_3$(s) within the 5 wt.% limits of detection of impurity phases by powder X-ray diffractometry. CaO was prepared by the thermal decomposition of $CaCO_3$ in air at 1273 K for 3 h. The ternary electrode used in the e.m.f. measurements was made by mixing CaO, $CaRuO_3$ and ruthenium in the mass ratio 3:4:2, followed by compacting into cylindrical pellets of diameter 10 mm and thickness 2 mm at a pressure of 100 MPa.

The following cell configuration was used for e.m.f. measurements:

$$\text{Pt, CaO, CaRuO}_3\text{, Ru} \,|\, \text{15 CSZ} \,|\, \text{O}_2\ (P_{O_2}=0.21\ \text{atm}),\ \text{Pt} \qquad (1)$$

15 CSZ represents a 15wt.%CaO-stabilized ZrO_2 cylindrical solid electrolyte tube (Corning, U.S.A.) with one end closed and the closed end flat conforming to the following dimensions: outer diameter, 12.7 mm; inner diameter, 9.8 mm; length, 350 mm. This tube electrolyte was used to separate the gaseous environments of the test electrode and the air–reference electrode compartments. Helium gas purified by passing through a trap containing refrigerated molecular sieves at a very low flow rate (less than 10^{-3} m^3 h^{-1}) provided the inert gas blanket for the cell assembly. Titanium sponge was employed as an *in situ* getter of oxygen in the vicinity of the electrode pellet. The temperature was measured by a Pt–10%Rh/Pt thermocouple calibrated at the freezing points of high purity tin, zinc, bismuth and silver. 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 change for the cell reaction. The e.m.f. readings were taken after equilibrating the galvanic cells at 950 K for at least 24 h. Only those cell voltages which did not drift by more than a fraction of a millivolt per hour and were reproducible during the subsequent heating cycles were taken into account. The internal consistency was checked by thermal cycling as well as by varying the ratio of the three coexisting phases of the test electrode to the extent of 10 wt.% from the mean ratio given above for different experimental runs. Reproducible e.m.f. values were recorded only above 950 K. The electrodes were examined by XRD at the end of each experiment to confirm the absence of change in phase composition. The details of purification of the helium cover gas, ensuring the absence of asymmetric potentials, temperature measurement and other experimental details are described in earlier publications [11–14].

3. Results and discussion

The e.m.f. results on cell (1) as summarized in Table 1 are graphically represented in Fig. 1. A least-squares analysis of the data in Table 1 had yielded the expression

TABLE 1

Experimental e.m.f. results for cell (1)[a]

Run	T (K)	E (mV)	T (K)	E (mV)	T (K)	E (mV)
1	1029.0	378.69	1096.6	352.35	1140.3	333.33
	1191.2	318.15	1005.4	387.03	1073.6	361.69
	1159.7	326.20	1212.5	308.88	1296.1	278.84
	1009.0	382.56	1083.7	355.89	1173.4	322.89
	1256.9	293.47	1078.7	362.56	1150.9	330.18
	1217.9	306.92	1280.0	284.96	971.4	399.28
	1039.3	372.12	1129.1	337.92	1196.5	314.00
	1282.8	284.35				
2	1050.5	370.55	1123.0	340.56	1191.5	317.02
	1274.3	286.96	1131.3	341.09	1197.7	315.03
	1241.6	302.02	1180.6	323.34	1232.6	302.51
	1311.8	273.04	1107.7	350.94	1168.3	324.43
	1239.2	299.35	1171.0	328.32		
3	1062.4	363.58	1153.7	334.13	1214.9	310.46
	1290.8	279.47	987.2	389.78	1100.8	352.13
	1174.3	323.95	1234.0	300.90	1305.2	274.02
	1131.6	339.12	1195.3	318.86	1153.4	330.27
	1204.5	313.19	1254.0	294.59	1305.0	276.01
	1117.0	342.82	1262.0	291.81	1209.8	307.83
	1285.5	284.39	1145.2	332.61	1182.1	319.74
	1220.5	308.66	1188.9	315.86	1263.0	293.39

[a] Pt, CaO, $CaRuO_3$, Ru|15 CSZ|O_2 ($P_{O_2}=0.21$ atm), Pt.

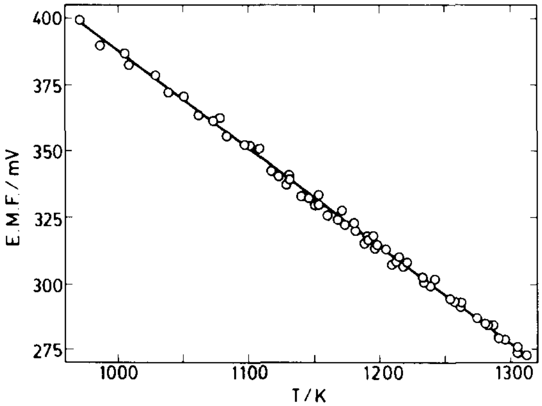

Fig. 1. Experimental e.m.f. results of the cell described by expression (1).

$$E_{(1)} = 754.16 - 0.36659T \pm 1.70 \text{ mV} \tag{2}$$

which is valid over the experimental range of measurement, namely from 971 to 1312 K. After connecting for the standard state of oxygen in the reference air electrode in cell (1), the overall cell reaction for the passage of 4 F of electricity could be represented as follows:

$$CaO(s) + Ru(s) + O_2(g) \rightleftharpoons CaRuO_3(s) \tag{3}$$

The corresponding standard Gibbs energy change ΔG_r^0 for reaction (3) was derived to be

$$\Delta G_r^0 = -291068 + 128.479T \pm 660 \text{ J mol}^{-1} \tag{4}$$

from the e.m.f. expression in eqn. (2) after correcting for the standard state of oxygen. For the standard Gibbs energy of formation ΔG_f^0 of RuO_2, Mallika and Sreedharan [15] had reported the expression

$$\Delta G_f^0(RuO_2) = -305464 + 172.70T \pm 1245 \text{ J mol}^{-1} \tag{5}$$

valid over the range 751–1200 K from e.m.f. measurements, which was assessed to be in good agreement with the other measurements reported earlier in the literature [16–19]. In order to derive the standard Gibbs energy of formation $\Delta G_{f,\text{ ox}}^0$ for the solid–solid reaction

$$CaO + RuO_2 \rightleftharpoons CaRuO_3 \tag{6}$$

eqns (3) and (4) were combined to yield

$$\Delta G_{f,\text{ ox}}^0 = 14396 - 44.221T \pm 1905 \text{ J mol}^{-1} \tag{7}$$

For such solid–solid reactions, one should expect the $\Delta S_{f,\text{ ox}}^0$ to be a small positive quantity of the order of 10 J mol^{-1} K^{-1} as against 44 J mol^{-1} K^{-1} observed in eqn. (7). This could be either due to not too high a reliability of the values of slopes in e.m.f. measurements [20] or due to the possibility of non-stoichiometry [21] and disorder in the structure of $CaRuO_3$. The C_P and $S_{f,\text{ 298}}^0$ data are not available on $CaRuO_3$ to assess the possible temperature-dependent errors in $\Delta G_{f,\text{ ox}}^0$ by the third-law method.

From the value of ΔG_r^0 given in eqn. (4), the equilibrium log P_{O_2} over the buffer mixture CaO–$CaRuO_3$–Ru was calculated to be

$$\log P_{O_2} = 6.712 - 15205/T \tag{8}$$

where P_{O_2} is in atmospheres and T in degrees kelvin. Equation (8) yields values of −8.49 atm and −4.98 atm for log P_{O_2} at 1000 K and 1300 K respectively. These values are about two orders of magnitude lower than the equilibrium oxygen pressure of an Ru–RuO_2 mixture at 1000 and 1300 K which explains the formation of $CaRuO_3$ instead of RuO_2 on heating a mixture of $CaCO_3$ and ruthenium in air at higher temperatures.

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