Thermochimica Acta, 129 (1988) 63–69
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE ENTHALPY OF FORMATION OF RuO_2

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ABSTRACT

The Gibbs energy of formation of $RuO_2(s)$ has been measured from 962 to 1070 K by the e.m.f. technique using $ZrO_2(+CaO)$ as the solid electrolyte. A "Third-Law" evaluation of the experimental results gives for the enthalpy of formation of $RuO_2(s)$ the value $-(314.15 \pm 0.02)$ kJ mol^{-1}. Previous values from the literature are discussed.

INTRODUCTION

In the binary system ruthenium–oxygen two solid oxides have been found to exist, RuO_2 and RuO_4. The latter compound is stable at room temperature, melts at 298.5 ± 0.5 K, and has a boiling point of 406 ± 5 K [1]. Thus, ruthenium dioxide is the only solid oxide at higher temperatures. It is a transition metal oxide with the rutile structure, having interesting electrical, magnetic, optical, and catalytic properties [2,3]. Moreover, since ruthenium is formed in high yields during the fission of uranium in a nuclear reactor, it also plays an important role in analysis of accidents in nuclear reactors.

The thermochemical properties of RuO_2 are poorly known, and the measured data show much discrepancy [1]. This is particularly true for the enthalpy of formation. As part of a systematic investigation of the thermodynamic properties of compounds of fission products, relevant to accident analysis, we also studied the thermochemical properties of RuO_2 [4]. We here present e.m.f. measurements from which, by "Third-Law" analysis, the enthalpy of formation of RuO_2 at 298.15 K has been derived.

EXPERIMENTAL

Sample preparation

Ruthenium dioxide was prepared as a deep-blue powder by the oxidation of $RuCl_3$ in oxygen gas at 675 K. Ruthenium trichloride was obained by the

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Dedicated to Professor Oswald Kubaschewski in honour of his contribution to thermochemistry.

0040-6031/88/$03.50

chlorination of ruthenium powder (99.9%) at 675 K for 4 h followed at 875 K for 1 h. The powder was analysed by reduction in hydrogen at 1125 K, and weighing the metal. The Ru content was 75.84 ± 0.02% (calc. 75.96%). The sample was, according to X-ray analysis, phase pure.

E.M.F. measurements

The measurements were carried out with $ZrO_2(+CaO)$ as the solid electrolyte in the reversible cell

$Ru,RuO_2/ZrO_2(CaO)/O_2$ ($p = 1$ atm)

Purified oxygen at about 1 atm, being the reference, was passed through an inlet tube into a gas-tight zirconia tube which was closed at one end. A pressed and sintered pellet of a mixture of Ru and RuO_2 powder (1 : 1) was placed outside the zirconia tube, and kept in good contact with the bottom of the tube. This compartment of the e.m.f. cell, contained within a quartz jacket, was evacuated and filled with purified argon gas.

Temperatures were measured with calibrated Pt/Pt + 10% Rh thermocouples, and read with a digital voltmeter (Solartron A200). At the electrodes, contacts of platinum, gold, or silver were used, but only in the case of silver was no diffusion of the metal into the ruthenium observed at the temperatures at which the cell was operated. E.M.F. values were read with a digital voltmeter (Solartron A200) after equilibrium was established. The times varied from at least 10 h (below 950 K) to within 1 h (above 1050 K). Equilibrium attainment was checked by measuring both after heating and cooling.

RESULTS

Three different series of measurements have been obtained, one with air (20.8% O_2) as the reference electrode, and the other with oxygen gas at about 1 atm. Barometric pressures were accurately measured during the measurements. The results of the measurements are given in Table 1. The net chemical reaction of the cell for the passage of 4 Faradays is

$$Ru + O_2 \rightarrow RuO_2$$

and, from $\Delta G^{\ominus}(T) = -4F \cdot E_{cell}$,

$$\Delta G_f^{\ominus}(RuO_2) = -4F \cdot E_{cell} + RT \ln p_{O_2}$$

From the values of $\Delta G_f^{\ominus}(RuO_2)$ thus obtained the enthalpy of formation at 298.15 K has been calculated by the "Third-Law" method. A recent determination of the entropy of RuO_2 from low-temperature heat capacity

TABLE 1

E.M.F. measurements of the cell Ru + $RuO_2/ZrO_2(+CaO)/O_2$, Gibbs energies of formation of RuO_2(s), and "Third-Law" enthalpies of formation. The experimental points are given in the order of measuring

T (K)	E (mV)	p_{O_2} (Pa)	$\Delta G_f^\ominus$ (kJ mol^{-1})	$\Delta H_f^\ominus$(298.15 K) (kJ mol^{-1})
Series 1; $p_{O_2} \simeq 2 \times 10^4$ Pa (air)				
988.1	316.2	20771	−135.054	−314.37
1013.5	304.4	20895	−130.782	−314.37
1038.7	292.3	20832	−126.471	−314.32
1063.9	280.5	20784	−122.268	−314.33
1034.3	294.0	20490	−127.214	−314.32
1008.8	306.0	20599	−131.459	−314.27
983.3	318.4	20942	−135.772	−314.28
				−314.32 ± 0.03
Series 2; $p_{O_2} \simeq 10^5$ Pa				
986.8	349.9	98712	−135.254	−314.35
1011.4	338.8	99645	−130.896	−314.15
1036.7	328.1	100245	−126.719	−314.23
1006.5	341.5	101925	−131.749	−314.18
				−314.23 ± 0.09
Series 3; $p_{O_2} \simeq 10^5$ Pa				
961.8	361.3	102592	−139.340	−314.20
986.2	350.0	101698	−135.048	−314.04
996.4	345.3	101538	−133.247	−313.97
1006.5	340.9	101418	−131.559	−313.99
1021.7	334.3	101378	−129.015	−314.00
1031.3	330.3	101632	−127.449	−314.05
1046.6	323.7	101818	−124.886	−314.06
1056.7	319.3	101885	−123.182	−314.04
1066.6	315.0	101898	−121.521	−314.04
1076.8	310.7	102018	−119.850	−314.07
1069.9	313.7	102072	−121.004	−314.07
1060.1	317.9	102058	−122.626	−314.06
1050.0	322.2	102005	−124.291	−314.03
1040.1	326.5	101978	−125.953	−314.03
1027.0	332.1	101965	−128.116	−314.00
1016.8	336.6	102125	−129.840	−314.00
1000.8	343.6	102058	−132.548	−314.01
1010.8	339.0	102005	−130.777	−313.93
993.8	346.5	102018	−133.671	−313.95
968.1	357.8	102898	−137.965	−313.89
978.2	353.4	102992	−136.258	−313.90
973.2	355.6	103072	−137.101	−313.89
946.9	367.2	103685	−141.535	−313.85
953.6	364.4	103685	−140.453	−313.91
940.4	370.3	104125	−142.700	−313.91
950.0	365.8	104058	−140.966	−313.81
959.6	361.9	104098	−139.456	−313.94
965.0	359.4	103645	−138.525	−313.92
				−313.98 ± 0.03

measurements [4], yielding $S^{\ominus}(298.15\text{ K}) = 56.42\text{ J mol}^{-1}\text{ K}^{-1}$, and a redetermination of the enthalpy increments of ruthenium metal [5]

$$\{H^{\ominus}(T) - H^{\ominus}(298.15\text{ K})\} = 21.5070(T/\text{K}) + 4.28133 \times 10^{-3}(T/\text{K})^2 - 6792.9$$

and of RuO_2 [4]

$$\{H^{\ominus}(T) - H^{\ominus}(298.15\text{ K})\} = 53.6440(T/\text{K}) + 20.19049 \times 10^{-3}(T/\text{K})^2 + 8.23298 \times 10^{5}(T/\text{K})^{-1} - 20550.1$$

enabled us to calculate the enthalpy of formation of $RuO_2(s)$ in this way. The entropy of ruthenium metal has been taken from the assessment by Furukawa et al. [6]; the free energy functions of oxygen gas have been calculated from equations given by Glushko et al. [7].

The weighted mean of the results, listed in Table 1, gives

$\Delta_f H^{\ominus}(298.15\text{ K}) = -314.15 \pm 0.02\text{ kJ mol}^{-1}$.

DISCUSSION

Previous determinations of the enthalpy of formation of RuO_2 have been reviewed by Rard [1], and the recommended value at 298.15 K (-307.2 ± 7.8 kJ mol^{-1}) was based on decomposition pressure measurements, e.m.f. measurements, and a value for the direction combination of ruthenium in oxygen (Table 2). For the evaluation of the enthalpy of formation of RuO_2 from the equilibrium measurements, Rard used—in the absence of a mea-

TABLE 2

The enthalpy of formation of $RuO_2(s)$ at 298.15 K

Authors	Technique	Temperature range (K)	$\Delta H_f^{\ominus}(298.15\text{ K})$ (kJ mol^{-1})	
			"Second-Law"	"Third-Law"
Remy and Köhn (1924) [8]	decomp.	1203	-219.7	
Shchukarev and Ryabov (1960) [9]	combustion		-305.4	
Schäfer et al. (1963) [10]	decomp.	1377–1451	-297.8 ± 1.5	-316.2 ± 3.5
Bell and Tagami (1963) [11]	decomp.	1380–1776	-302.1 ± 8.5	-310 ± 1
Kleykamp (1969) [12]	e.m.f.	780–1040	-311.7 ± 4.2	-316 ± 4
Pizzini and Rossi (1971) [14]	e.m.f.	1170–1523	$-$ [a]	-312.5 ± 1.5
Chatterji and Vest (1971) [15]	e.m.f.	873–1273	-298.9 ± 0.84	-317.2 ± 0.4
Tagirov et al. (1975) [18]	mass spectr.	1000–1200	-306.3 ± 6.30	-317.8 ± 1.5
Present results	e.m.f.	962–1070		-314.15 ± 0.02

[a] -306.9 kJ mol^{-1} at 985 K.

sured entropy of RuO_2—a modified Second-Law method. As usual, much scatter in the extrapolated values was obtained, and the uncertainty in the assessed value was likewise high.

Since experimental values for the entropy of RuO_2 and the heat capacities of Ru and RuO_2 are available now [4,5], we have recalculated these measurements using the "Third-Law" method; the results are also given in Table 2.

The enthalpy of formation RuO_2 as given in the literature up to 1960 was based on dissociation pressure measurements by Remy and Köhn [8], dating from 1924. But in 1960 Shchukarev and Ryabov [9] measured the enthalpy of formation of RuO_2 by direct combustion of ruthenium, and obtained a value of -305.4 ± 4.2 kJ mol^{-1}, which was much more negative than the value -219.7 kJ mol^{-1} hitherto accepted.

Schäfer et al. [10] remeasured the decomposition pressures using several techniques and showed that the pressures, measured by Remy and Köhn, must have been too high. They showed that included gas could have played a role in the static pressure measurements and, as a consequence, recommended their oxygen pressures at three different temperatures measured dynamically with a thermobalance. When we recalculate the enthalpy of formation at 298.15 K from these measurements, we do not get a defined value, but values ranging from -313 to -316 kJ mol^{-1}.

Almost at the same time, Bell and Tagami [11] measured oxygen decomposition pressures of the system both statically and dynamically, the results from both techniques being in perfect agreement. They calculated the enthalpy of formation of RuO_2 at 298.15 K using estimated entropy and heat capacity values. A recalculation of their data (no individual points were given) yields a slightly changing value for $\Delta H_f^\ominus$(298.15 K) varying from -309 (at 1100 K) to -310.8 kJ mol^{-1} (at 1500 K).

A different approach came from three different groups of investigators who measured, almost at the same time, the thermodynamic stability of RuO_2 with the same technique: a reversible galvanic cell. Kleykamp [12] used a mixture of Fe,FeO as the reference electrode, but did not give individual, experimental e.m.f. values. We recalculated his $\Delta G_f^\ominus(RuO_2)$ equation, using $\Delta G_f^\ominus$(FeO) from a recent assessment by Spencer and Kubaschewski [13], and obtained from this equation values for the enthalpy of formation of RuO_2 at 298.15 K ranging from -320.0 (at 800 K) to -312.4 kJ mol^{-1} (at 1050 K). Pizzini and Rossi [14] used air as the reference electrode. From their $\Delta G^\ominus$ equation as a function of T we calculate values for $\Delta H_f^\ominus(RuO_2)$ at 298.15 K ranging from -313.7 (800 K) to -311.1 kJ mol^{-1} (1200 K). Finally, Chatterji and Vest [15] used a mixture of Cu and Cu_2O as the reference electrode. We recalculated their $\Delta G_f^\ominus(RuO_2)$ equation, using $\Delta G_f^\ominus(Cu_2O)$ from an assessment by Santander and Kubaschewski [16], and obtained values for $\Delta H_f^\ominus(RuO_2)$ at 298.15 K varying from -316.8 (900 K) to -317.6 kJ mol^{-1} (1200 K).

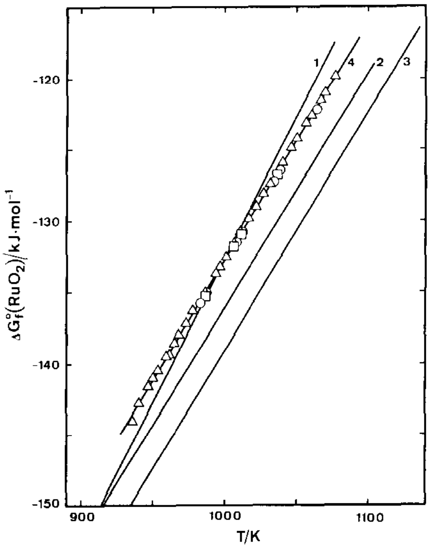

Fig. 1. The Gibbs energies of formation of RuO_2(s), as obtained from e.m.f. measurements. 1, Kleykamp [12]; 2, Chatterji and Vest [15]; 3, Pizzini and Rossi [14]; 4, present results; ○, series 1; □, series 2; △, series 3.

In Fig. 1 the three e.m.f. measurements from literature are compared with our measurements. Kleykamp's results show a different slope, and $\Delta H_f^{\ominus}$(298.15 K) values which are not constant within the limits of uncertainty, but change as a function of temperature. This indicates that other electrode processes have also taken place. The measurements of Pizzini and Rossi, and of Chatterji and Vest do have the same slope, but their $\Delta H_f^{\ominus}$(298.15 K) values differ somewhat from ours, in all probability because they are influenced by the dissolution of ruthenium into the platinum contact at the Ru/RuO_2 electrode. Hutchinson [17] showed the solid solubility of ruthenium in platinum to be very high, about 62 atm% at 1000 °C. This indicates that the use of platinum contacts will lead to erroneous results.

Finally, Tagirov et al. [18] measured the decomposition pressures of RuO_2(s) by mass spectrometry in the range 990–1190 K, yielding $\Delta H_f^{\ominus}$(298.15 K) = -315.9 (at 1000 K) to -318.6 kJ mol^{-1} (at 1200 K).

It can be concluded that most of the measurements from the literature, after recalculation, give values for the enthalpy of formation of RuO_2(s) ranging from -310 to -320 kJ mol^{-1}. The only calorimetric value $\Delta H_f^{\ominus}$(298.15 K) = -305.4 kJ mol^{-1} [9] is probably too high because of incomplete combustion. The value derived from our e.m.f. measurements -314.15 ± 0.02 kJ mol^{-1} is in fair agreement with these measurements. As Professor Kubaschewski has often emphasized (for instance, in the article reprinted in this volume), e.m.f. measurements can give the high accuracies obtained here, provided experimental errors can be eliminated.

ACKNOWLEDGEMENTS

The authors wish to thank Mrs. W. Ouweltjes and A. Booy for experimental assistance.

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