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THE ENTHALPY OF FORMATION OF IrO_2 AND THERMODYNAMIC FUNCTIONS

E.H.P. CORDFUNKE

Netherlands Energy Research Foundation ECN, Petten (The Netherlands)

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ABSTRACT

The Gibbs energy of formation of $IrO_2(s)$ has been measured by means of oxygen dissociation pressure measurements, and by EMF measurements using ZrO_2 (+ CaO) as the solid electrolyte. In addition, high-temperature enthalpy increments of IrO_2 have been measured from 416 to 940 K using a drop calorimeter. A "third law" evaluation of the experimental results and data from literature has been made. For the enthalpy of formation of $IrO_2(s)$ the value $\Delta H_f^0(298.15\ K) = -(59.60 \pm 0.03)$ kcal $mole^{-1}$ has been selected. The thermodynamic functions of $IrO_2(s)$ have been calculated in the temperature range 298—1200 K.

INTRODUCTION

Iridium has excellent high-temperature properties in inert atmospheres. In the presence of oxygen, however, rapid oxidation occurs, together with volatilization of $IrO_3(g)$ and $IrO_2(g)$ as the major volatile species [1—4]. A knowledge of the thermodynamics of the iridium—oxygen system is thus important in understanding the high-temperature behaviour of the element.

There is an abundance of published experimental data pertaining to the thermochemistry of this system. Notwithstanding this fact the agreement between the various investigations is only poor. This is particularly true for the determination of the enthalpy of formation of the only solid oxide, IrO_2. Attempts to measure this quantity cover a period of more than 100 years. The first measurements of the dissociation pressure of $IrO_2(s)$ originate from Sainte-Claire Deville and Debray in 1878 [5]. Since that time many others have investigated the equilibrium $Ir + O_2 = IrO_2(s)$, by dissociation pressure measurements [6—9], EMF measurements [10,11], and by calorimetry [12]. The enthalpies of formation of $IrO_2(s)$ at 298.15 K derived from these measurements show a considerable scatter, ranging from —40 to —65.6 kcal $mole^{-1}$. Part of the scatter arises from a lack of accurate heat capacity data which made an assessment by second- and third-law evaluation almost impossible. This paper reports new measurements of the high-temperature enthalpy contents of IrO_2, dissociation pressures and EMF values. Together with data from literature, including low-temperature heat capacities, a consistent picture of the thermodynamic properties of $IrO_2(s)$ has been obtained, and will be presented here.

EXPERIMENTAL

Sample preparation

IrO_2 was prepared as a deep-blue powder by the oxidation of $IrCl_3$ (which was prepared by the chlorination of iridium powder at about 600°C) at 1000°C in oxygen overnight. The degree of crystallinity of IrO_2 depends largely on the temperature and the duration of the oxidation. The direct oxidation of iridium powder does not give complete oxidation to IrO_2.

IrO_2 was analysed from the weight loss by reduction in hydrogen at about 400°C. The iridium content of the sample used was 86.04% (calcd. 85.73%).

Drop calorimeter

High-temperature enthalpy increments were measured between 400 and 900 K in a diphenylether drop calorimeter, as described in detail previously [13]. A sample of 10.290 g of IrO_2 was encapsulated in a silica bulb of 2.026 g SiO_2. The enthalpy of the IrO_2 is thus more than 60% of the total at all temperatures. The difference between the values of $\{H^0(T) - H^0(T')\}$, in which T' is the temperature of the calorimeter, for the loaded and the empty quartz glass capsule can be calculated, and gives, after a correction for $(T' - 298.15\ \mathrm{K})$ with the C_p value, the values of $\{H^0(T) - H^0(298.15\ \mathrm{K})\}$ for the specimen. The results are given in Table 1.

Dissociation pressure measurements

The oxygen pressures of the equilibrium

$$Ir + O_2 = IrO_2(s)$$

were measured in a closed quartz tube connected with a mercury manometer, as described earlier [7]. Before the measurements the apparatus was

TABLE 1

Calorimetric enthalpy measurements

T (K)	$H^0(T) - H^0$ (298.15 K) (cal mole^{-1})		δ (cal mole^{-1})
	Exp.	Calcd.	
416.0	1 697	1 699	−2
431.5	1 936	1 938	−2
456.1	2 321	2 322	−1
579.7	4 337	4 340	−3
613.8	4 918	4 919	−1
659.6	5 709	5 708	1
701.6	6 459	6 445	14
827.0	8 697	8 711	−14
895.7	9 993	9 991	2
936.9	10 774	10 771	3

TABLE 2

Oxygen pressures of the equilibrium $Ir(s) + O_2(g) = IrO_2(s)$
Gibbs energies of formation of $IrO_2(s)$, and "third law" enthalpy of formation

T (K)	p_{O_2} (mm)	ΔG_f^0 (kcal mole^{-1})	ΔH_f^0(298.15 K) (kcal mole^{-1})
1114.9	6.43	−10.573	−59.621
1115.4	6.46	−10.568	−59.635
1116.3	6.62	−10.522	−59.627
1124.1	7.64	−10.275	−59.704
1141.5	11.07	−9.593	−59.748
1142.9	11.18	−9.582	−59.794
1151.7	13.46	−9.231	−59.812
1164.0	18.10	−8.645	−59.737
1172.5	21.87	−8.267	−59.712
1179.1	26.24	−7.887	−59.605
1180.6	25.80	−7.937	−59.717
1193.0	33.64	−7.391	−59.687
1200.9	39.05	−7.084	−59.705
1204.1	40.93	−6.990	−59.744
1206.9	46.15	−6.719	−59.589
1215.5	53.21	−6.423	−59.649
1215.5	53.37	−6.416	−59.642
1223.3	60.74	−6.142	−59.690
1237.7	80.24	−5.530	−59.672
1239.9	83.93	−5.429	−59.663
1242.7	91.22	−5.235	−59.584
1249.0	100.42	−5.023	−59.631
1257.2	116.27	−4.690	−59.638
1262.0	126.24	−4.502	−59.648
1268.2	140.22	−4.259	−59.660
1271.2	145.43	−4.177	−59.700
		Mean value: ΔH_f^0(298.15 K) = −(59.68 ± 0.01)	

thoroughly evacuated, after which the furnace was heated to the desired temperature. It was checked by pumping off that equilibrium oxygen pressures were measured. The results are given in Table 2.

EMF measurements

The measurements were carried out with ZrO_2 (+CaO) as the solid electrolyte. A gas-tight tube of zirconia, closed at one end, was contained within a quartz jacket. Oxygen of 1 atm pressure was used as reference, and was passed through the quartz tube outside the zirconia tube. A pellet of a mixture of iridium metal powder and IrO_2 powder was placed inside the zirconia tube, and kept in good contact with the flat bottom of the tube by means of a closed quartz thermocouple jacket. The inner compartment of the EMF cell could be evacuated and filled with purified argon gas. Temperatures were measured with a calibrated Pt/Pt,13% Rh thermocouple, and read with a digital voltmeter (Solartron A210).

Preliminary experiments with pellets of a mixture of nickel metal powder and NiO powder as the reference electrode in the outer compartment failed because of reaction between the nickel leads and the iridium metal in the inner compartment. For this reason the (Ni + NiO) electrode was replaced by oxygen, and the nickel contacts by Au contacts. No reaction was observed in this case.

X-Ray diffraction measurements

All samples were checked for phase purity using a Guinier—De Wolff camera with CuK_α radiation. Lattice parameters were measured with a Philips back reflection camera using W-powder as internal standard.

RESULTS *

Enthalpy increments

The results of the drop-calorimetric measurements are given in Table 1. Over the range of measurements the enthalpy increments as a function of temperature can be represented by the polynomial expression of the usual form $aT + bT^2 + cT^{-1} + d$, the coefficients of which have been obtained by least squares. The boundary conditions were applied such that, when $T = 298.15$ K, $\{H^0(T) - H^0(298.15\text{ K})\} = 0$, and $C_p(T) = C_p(298.15\text{ K})$. The last quantity has been obtained from low-temperature heat capacity measurements by Westrum [14], giving $C_p(298.15\text{ K}) = 13.30$ cal deg^{-1} mole^{-1}.
We now obtain, in the interval 298—937 K.

$$\{H^0(T) - H^0\ (298.15\text{ K})\}/\text{cal mole}^{-1} = 14.7874\ (T/\text{K}) + 2.4386.10^{-3}(T/\text{K})^2 + 2.6148.10^5\ (T/\text{K})^{-1} - 5502.6$$

The only heat capacity measurements available for IrO_2 are those by Wöhler and Jochum [12]. However, Bell et al. [9] pointed out that these results seem unlikely and, based on a comparison with a number of MO_2(s) compounds, suggested a different formula for the heat capacity of IrO_2(s). When we compare the C_p values derived from our measurements with those by Wöhler and Jochum (after a correction for the atomic mass of iridium), it appears that our values are lower than Wöhler's, the difference rapidly increasing from 0.5% at 400 K to 12% at 700 K. It is also evident that Bell's estimate gives a better approximation of the heat capacity of IrO_2(s).

Oxygen dissociation pressure measurements

Wöhler and Witzmann [6] were the first to show that when starting the experiments with a fresh sample of IrO_2 the oxygen pressure of the equili-

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* Throughout this paper, 1 cal = 4.184 J.

brium IrO_2 + Ir does not have a constant value but is lowered by pumping off the oxygen. A constant value is obtained, according to Cordfunke and Meyer [7], when the phase boundary of the two-phase equilibrium IrO_{2-x} + Ir is reached. Since these experiments, other investigators have measured the dissociation equilibrium by various techniques. Bell et al. [9] concluded, based on their measurements, that the composition of $IrO_2(s)$ deviates little, if any, from stoichiometry in the temperature range 800—1050° C and they measured the oxygen pressures as a function of temperature using a static method. Their results support previous measurements by Schneidereit [8], who also did not find indications for deviations from stoichiometry. For this reason we decided to reinvestigate the dissociation equilibrium. When starting the oxygen pressure measurements with a freshly prepared pure sample of IrO_2, it was again found that the initial oxygen pressure can be lowered by pumping off; this can be repeated until reproducible values are obtained.

The lattice parameter of this sample has been measured accurately by a back reflection X-ray technique, and compared with lattice parameters of the original sample, and with that of an equimolar mixture of (IrO_2 + Ir) heated for 17 h at 950°C. This mixture has also been heated to ~1000°C in a high-temperature X-ray camera (Guinier—Lenné camera), and compared with a similar exposure of a pure IrO_2 sample under the same conditions. After the exposures the quartz pattern was taken on the films at room temperature. This enables us to calculate the lattice parameters of the IrO_2 samples at any temperature between room temperature and 1000° C.

From the results, no indications for a solid solution behaviour of iridium in IrO_2 could be found, the lattice parameters of the various samples in a group of experiments being identical within the limits of accuracy. This conclusion is in disagreement with our previous observations [7]. The reason for this is not quite clear, but may be found in the fact that the present X-ray technique used is more powerful.

When we accept that $IrO_2(s)$ has little or no range of stoichiometry, it remains to be explained why the oxygen pressure can be lowered by pumping off. We have to assume that small amounts of oxygen can be adsorbed strongly on the IrO_2, even up to the high temperatures of the measurements.

Table 2 gives the results of the measurements of the equilibrium Ir + O_2 = $IrO_2(s)$. The results can be expressed as

$$\log p_{O_2}(\mathrm{mm}) = \frac{-(12518 \pm 62)}{T} + (12.021 \pm 0.052)$$

From this it follows that the enthalpy of the reaction at the mean temperature of the measurements $\Delta H^0_{1192} = -(57.280 \pm 0.280)$ kcal mole^{-1}. For the "second law" enthalpy of formation of IrO_2, we then find $\Delta H^0_{298} = -(60.17 \pm 0.28)$ kcal mole^{-1} using the enthalpy increments of IrO_2, as given before, and the enthalpy increments of iridium [15] and oxygen [16].

It is now also possible to calculate the "third law" enthalpy of formation of IrO_2 using the entropy of IrO_2: $S^0_{298} = 12.192$ cal deg^{-1} mole^{-1}, as determined by Westrum [14]. The calculation gives ΔH^0_f (IrO_2,s,298.15 K) = $-(59.68 \pm 0.01)$ kcal mole^{-1}, in fair agreement with the "second law" enthalpy given previously.

EMF measurements

Two different types of EMF cells have been used to measure the thermodynamic stability of IrO_2:

(1) Ir, IrO_2/ZrO_2, CaO/Ni, NiO;

(2) Ir, IrO_2/ZrO_2, CaO/O_2 (p = 1 atm).

It appeared that in cell type (1) the nickel leads caused severe attack of the Ir + IrO_2 electrode. Because platinum reacts with both electrodes, we decided to take gold leads and oxygen (p = 1 atm) as the reference electrode. With this cell type stable EMF values have been rapidly obtained (within a few hours). The results, given in Table 3, can be represented by

$$\mathrm{EMF(mV)} = (0.468 \pm 0.002)\ T - (634.9 \pm 2.1)$$

The net chemical reaction of the cell for the passage of 4 Faradays is

$$2\ \mathrm{Ir} + \mathrm{O_2} = \mathrm{IrO_2}$$

From $\Delta G^0(T) = -4\ \mathrm{F}.E_{\mathrm{cell}}$ it is found

$$\Delta G^0(T)/\mathrm{cal\ mole^{-1}} = \Delta G_f^0(\mathrm{IrO_2}) = (43.170 \pm 0.184)\ T - (58\,566 \pm 194)$$

For the enthalpy of formation of IrO_2 at 298.15 K, $\Delta H_f^0 = -(60.93 \pm 0.19)$ kcal $mole^{-1}$ is obtained by "second law" evaluation, and by "third law"

TABLE 3

Electromotive force E of the cell Ir + $IrO_2/ZrO_2(+CaO)/O_2$ (p = 1 atm), Gibbs energies of formation of $IrO_2(s)$, and "third law" enthalpy of formation

T (K)	E (mV)	ΔG_f^0 (kcal $mole^{-1}$)	ΔH_f^0(298.15 K) (kcal $mole^{-1}$)
937.3	197.3	−18.200	−59.771
971.4	180.5	−16.650	−59.667
974.9	179.9	−16.595	−59.759
989.2	170.4	−15.718	−59.488
1019.4	158.0	−14.574	−59.616
1020.4	157.4	−14.519	−59.604
1038.1	148.4	−13.689	−59.519
1054.4	141.5	−13.052	−59.565
1060.2	138.2	−12.748	−59.506
1068.7	134.8	−12.434	−59.549
1091.7	123.8	−11.419	−59.497
1100.9	119.2	−10.995	−59.456
1106.6	116.8	−10.774	−59.473
1127.5	107.2	−9.889	−59.460
1133.8	104.0	−9.593	−59.428
1146.2	98.7	−9.104	−59.454
1158.4	93.0	−8.579	−59.437
1181.0	82.3	−7.592	−59.390
1220.5	64.6	−5.959	−59.391
			Mean value: ΔH_f^0(298.15 K) = −(59.53 ± 0.03)

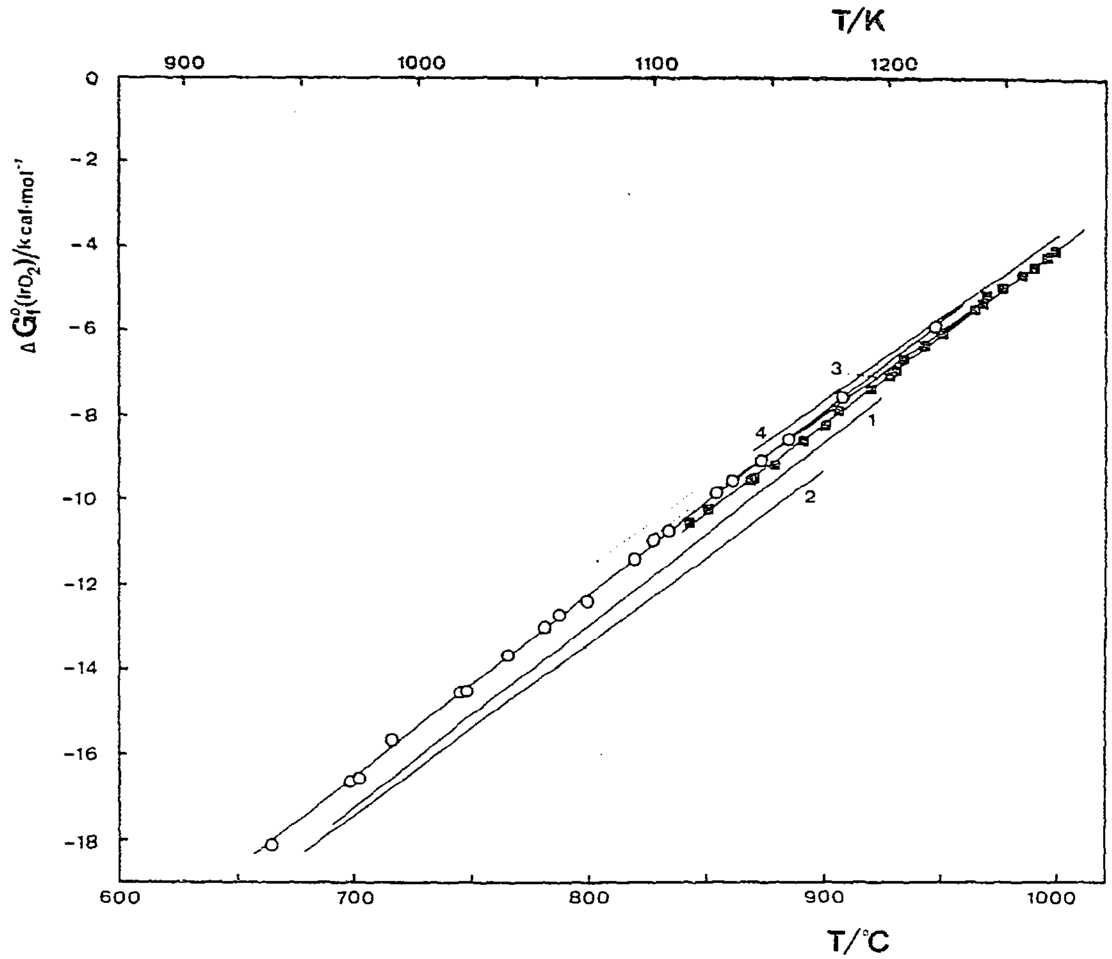

Fig. 1. The Gibbs free energy of formation of $IrO_2(s)$ as a function of temperature. ○, EMF measurements; ▣, dissociation pressure measurements; 1, Kleykamp and Paneth [10]; 2, Ramakrishnan et al. [11]; 3, Bell et al. [9]; 4, Cordfunke and Meyer [7].

evaluation $\Delta H_f^0 = -(59.53 \pm 0.03)$ kcal mole^{-1}, in perfect agreement with our dissociation pressure measurements.

Previous EMF measurements by Kleykamp and Paneth [10], and in particular those by Ramakrishnan et al. [11], yield somewhat lower values for the Gibbs energy of formation of IrO_2 (Fig. 1).

DISCUSSION

The existing literature gives values for the enthalpy of formation of IrO_2 which show a considerable scatter, varying from −40 kcal mole^{-1} [12] to −65.5 kcal mole^{-1} [17]. Since much of this scatter could be explained as a result of the "second law" treatment of the experimental results, we have recalculated all the existing experimental material by a "third law" treatment, using Westrum's entropy value of IrO_2. The results are listed in Table 4. It is evident that most of the scatter has now disappeared. Exceptions are

TABLE 4

The enthalpy of formation of $IrO_2(s)$ at 298.15 K

Refs.	ΔH_f^0 (kcal mole^{-1})(recalculated)		Method
	"Second law"	"Third law"	
5	−53.0	−60.0	Diss. pressure
12	−40.14		Calorimetry
7	−56.8	−59.3	Diss. pressure
8	−48.5	−59.8	Diss. pressure
9	−57.4	−59.7	Diss. pressure
10	−61.7	−60.3	EMF
11	−59.0	−60.7	EMF
	−60.6	−61.0	
18	−53.8	−56.6	Mass spectrometry
This work	−60.9	−59.5	EMF
This work	−60.2	−59.7	Diss. pressure

the mass spectrometric data by Kazenas et al. [18] in the temperature range 760—850 K and, to a less extent, the EMF measurements by Kleykamp and Paneth [10], and by Ramakrishnan et al. [11]. Apparently, small changes in the slope of the linear ΔG^0 functions, caused by impurities in the sample, and/or experimental errors, such as reactions at the electrodes in the EMF measurements or small amounts of absorbed oxygen in the vapour pressure measurements, cause considerable deviations in the intercept at 298 K, as obtained by "second law" calculations.

The only calorimetric value, ΔH_f^0 (298.15 K) = −40.14 kcal mole^{-1}, is in all probability in error because the other enthalpies of formation obtained by the authors [12] have appeared to be also in error.

When we take for the enthalpy of formation of IrO_2 the average value from our present results, we obtain ΔH_f^0 (298.15 K) = −(59.60 ± 0.03) kcal

TABLE 5

Molar thermodynamic properties of IrO_2

T (K)	$H_T - H_{298.15}$ (cal mole^{-1})	S^0 (cal K^{-1} mole^{-1})	ΔH_f^0 (kcal mole^{-1})	ΔG_f^0 (kcal mole^{-1})
298.15	0	12.192	−59.60	−46.09
300	25	12.272	−59.60	−46.01
400	1 456	16.379	−59.48	−41.49
500	3 024	19.872	−59.26	−37.02
600	4 684	22.896	−58.99	−32.60
700	6 417	25.567	−58.67	−28.22
800	8 215	27.967	−58.33	−23.90
900	10 072	30.153	−57.96	−19.62
1000	11 985	32.168	−57.57	−15.38
1100	13 952	34.043	−57.15	−11.18
1200	15 972	35.800	−56.71	−7.02

mole^{-1}. This value, which lies within the scatter of most of the literature data, has been selected to calculate the thermodynamic properties of IrO_2, as given in Table 5.

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