The Free Energies of Formation of WO_2 and MoO_2

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The standard molar free energies of formation of WO_2 and MoO_2 have been determined in the temperature range 1150—1450°K by means of a doped zirconia cell. The method differed only in details from that used by Taylor and Schmalzried.[1] The sample was contained in a small sintered aluminium oxide crucible which could be moved within the hot zone so as to allow fine adjustment of the sample temperature, which was measured by means of a separate thermocouple (*cf.* Fig. 1). The atmosphere at the commencement of each run was argon purified over calcium metal at 550°C and then saturated with water vapour at room temperature. A correction of the measured emf:s for changes in barometric pressure was included in the calculations.

Test runs. The apparatus was tested on the two systems iron-wüstite and Co—CoO. From the experimental values of $\Delta G°$ and T, linear equations were calculated by the least-squares method. In Tables 1 and 2 $\Delta G°$ values calculated from these equations at selected temperatures are listed together with those of corresponding figures obtained by previous investigators.

The system $W—WO_2$. W and WO_2 prepared[5] from H_2WO_4 (Merck, "Wolframsäure, reinst") were mixed in tungsten-oxygen ratios of 2:1, 1:1, and 2:3 and heated to 950°C for 48 h in sealed silica tubes.[6] After brief heating to 1200°C the samples gave stable emf values. A least-

Table 2. The standard free energy of formation of CoO (kcal/mole O_2).

	1073	1173	1273°K
This work [a]	−75.4	−72.3	−69.1
Taylor and Schmalzried [1]	−75.0	−71.6	−68.2
Coughlin [3]	−74.9	−71.2	−67.6
Kiukkola and Wagner [4]	—	−72.6	−69.2

[a] 13 free energy values were used in calculating the linear function.

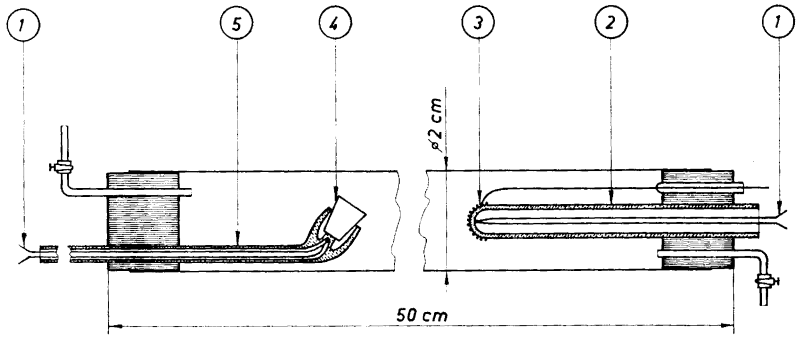

Fig. 1. 1, Thermocouple (PtRh/Pt). 2, Zirconia tube (Degussa ZR 23), 3, Platinum wire in contact with porous platinum layer. 4, Crucible. 5, Crucible holder (silica).

Table 1. The standard free energy of formation of wüstite (kcal/mole O_2).

	1073	1173	1273	1373	1473°K
This work [a]	−92.5	−89.7	−86.8	−84.0	−81.1
Taylor and Schmalzried [1]	−92.8	−89.6	−86.5	−83.4	−80.2
Darken and Gurry [2] as calculated in Ref. 1	−93.00	−89.76	−86.68	−83.52	−80.42

[a] 23 free energy values were used in calculating the linear function.

squares treatment of the data from the three runs (23 free energy values) yielded for the reaction

$$W(s) + O_2(g) = WO_2(s)$$

$$\Delta G^\circ_{1150-1450} = (-130.69 + 0.03584\ T)$$

kcal/mole.

The mean deviation was 0.24 kcal/mole. There was no significant difference between the runs. ΔG° values calculated from the equation at three temperatures are listed in Table 3 together with the results of previous investigators.

Table 3. The standard free energy of formation of WO_2 (kcal/mole O_2).

	1200	1300	1400°K
This work	−87.7	-84.1_5	−80.6
Kubaschewski and Evans [7]	−87.7	−84.0	−80.4
Barbi [8]	−88.79	—	—
Griffis [9]	−88.25	−84.26	−80.20
Rizzo, Bidwell and Frank [10]	−88.58	(−84.51) [a]	—
Rezukhyna and Golovanova [11]	−88.04	−83.79	(−79.55) [a]

[a] =extrapolated values.

The system Mo—MoO_2. Mo and MoO_2 were prepared [12,13] from molybdic acid ("Baker Analyzed"). Reduction to the metal of a dioxide sample gave a weight decrease corresponding to an original composition $MoO_{1.986}$. The samples used in the experiment were mixtures of metal and oxide in approximately equal proportions. Three runs (16 free energy values) yielded for the reaction

$$Mo(s) + O_2(g) = MoO_2(s)$$

$$\Delta G^\circ_{1150-1450} = (-134.99 + 0.03848\ T)$$

kcal/mole.

The mean deviation was 0.15 kcal/mole. ΔG° values calculated from the equation are listed in Table 4 together with the results of previous investigators.

Table 4. The standard free energy of formation of MoO_2 (kcal/mole O_2).

	1200	1300	1400°K
This work	−88.8	−85.0	−81.1
Kubaschewski and Evans [7]	−90.1	−86.2	−82.2
Barbi [8]	−87.35	—	—
Gleiser and Chipman [14]	−89.67	−85.66	−81.64
Schick [15]	−89.000	−84.968	−80.972

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