CLI.—*The Oxidation of Tungsten: Evidence for the Complexity of Tungstic Oxide,* WO_3.

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The rate of oxidation of a metal such as tungsten is governed by the rate of diffusion of oxygen through the protective layer of tungstic oxide formed upon the metal as a result of the reaction. In these circumstances the oxidation law is parabolic, *i.e.*, $W^2 = Kt$, where W is the weight of oxygen absorbed in time t, and K is a constant (Pilling and Bedworth, *J. Inst. Metals*, 1923, **29**, 529). For most metals K increases regularly with temperature according to the equation $K = Ae^{-Q/R\theta}$, where A and Q are constants, θ is the absolute temperature, and e and R have their usual significance (Dunn, *Proc. Roy. Soc.*, 1926, *A*, **111**, 207).

Since the properties of tungstic oxide determine the rate of oxidation of tungsten, abnormal variations in the latter are symptomatic of abnormal changes in the former. During the course of an investigation of the action of air upon tungsten at temperatures between 700° and 1000°, the rate of oxidation was found to vary abnormally between 850° and 900°. This is shown by the following values of K (in g.^{2}/cm.^{2} per hour) and by Fig. 1, in which log K is plotted against $1/\theta$.

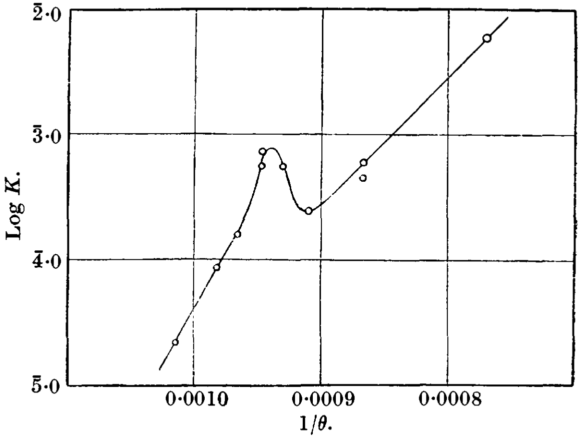
Temp. (C.)	700°	800°	850°	875°	900°	925°	950°	1000°
$K \times 10^5$	1·61	16·6, 22·5	40	18·0	17·9, 13·4	62·5	116	461

It was suspected at first that the oxide was undergoing a sintering action at temperatures above 850°, giving in consequence a less permeable oxide film. Such phenomena have been encountered in the cases of aluminium, copper, and zinc (Pilling and Bedworth, *loc. cit.*; Dunn, *loc. cit.*, pp. 207, 215), but in these cases the form of the oxidation curve during sintering undergoes modification and is no longer a quadratic parabola with respect to time, whereas, for tungsten at 875°, the parabolic law was obeyed perfectly, as may be seen from the constancy of K (in g.^{2}/cm.^{2} per hour) for the oxidation at this temperature :

t (mins.)	10	20	30	50	60	80	90	105	120	170
$K \times 10^4$	1·87	1·69	2·02	1·95	1·94	2·02	1·94	1·93	1·93	2·18

It is therefore certain that the tungstic oxide is in equilibrium from the commencement of the experiment. The only hypothesis in accordance with the facts is that tungstic oxide is not a pure unary substance but consists of a mixture of α-WO_3 and β-WO_3, the equilibrium between the two modifications shifting with temperature. The β-modification, which is formed in excess at higher temperatures, is less permeable to oxygen than the α-form, and in the temperature range in which the change from excess of β to excess of α occurs, a kink is found in the oxidation–temperature curve.

Fig. 1.



Some support for this hypothesis is afforded by the colour of the oxide : at the ordinary temperature it is lemon-yellow, but at higher temperatures it changes to quite a deep orange.

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