and the present results confirm this finding over a very wide pressure range, after 150 min of oxidation he reports the weight gain with 100 Torr oxygen pressure to be about only one quarter of the weight gain found at 10^{-2} Torr. It is difficult to explain the discrepancy between the two sets of data. Part of the discrepancy may be due to the different compositions of iron used and different methods of preparation.

The reason for the induction period observed at 5×10^{-6} Torr for both 350° and 400°C is probably either to a slow nucleation process (10) taking place or the removal of oxidizable impurities, most likely carbon from the specimen. Micrographs of replicas of oxide surfaces at the end of the induction period are shown in Fig. 10 (d) and (e), where the growth of nuclei into a continuous film is taking place. As seen in Fig. 6, the induction period appears to be longer at 400°C than at 350°C, but the times involved are not sufficiently reproducible to unequivocably make such a distinction. Sewell (11) using an x-ray technique to study the kinetics of oxidation has also observed an induction period for the oxidation of (100) iron at 400°C and 3×10^{-6} Torr oxygen. It is also noteworthy that the oxide thickness determined using this new technique correlates well with the present microbalance data.

The parabolic plots shown in Fig. 7, 8, and 9 indicate two distinct regions of conformity; an initial good parabolic fit of the data, the oxidation rate increasing with increasing pressure and the duration of the agreement becoming shorter as the pressure is increased from 10^{-4} to 60 Torr. The initial parabolic behavior is followed by an intermediate stage before a second parabolic region is reached where the plots are approximately parallel, signifying that this second region is essentially independent of pressure. The two distinct parabolic rates are most clearly observed in Fig. 7, and the values of the rate constants derived from the data in this figure are the most accurate obtained; the actual values of the initial rate constants at 10^{-4}, 10^{-3}, and 10^{-2} Torr oxygen pressure and 350°C are 1.9×10^{-13}, 4.3×10^{-13}, and 1.35×10^{-12} g^2cm^{-4} sec^{-1}, respectively. In this parabolic region at 350°C and during the initial parabolic region at 400°C (Fig. 8), we are probably dealing solely with the growth of Fe_3O_4. The electron diffraction analysis of oxides formed after short times of oxidation at 10^{-3} Torr shows only Fe_3O_4 to be present (Table II), supporting this view. Thus, if initially we are only concerned with the growth of magnetite, then the rate of oxidation as given by the parabolic rate constant should be proportional to the concentration of cation vacancies at the oxide-oxygen interface, which in turn is proportional to the (oxygen pressure)$^{1/2}$. As the pressure is increased more oxygen is incorporated into the oxide and so more cation vacancies are formed, leading to enhanced diffusion of iron through these cation vacancies giving rise to an increased oxidation rate. It may be seen in Fig. 11 that for the oxidation at 10^{-4}, 10^{-3}, and 10^{-2} Torr and 350°C, the parabolic rate constant, taken from the initial slopes of the curves in Fig. 7, is proportional to the (pressure)$^{1/2}$.

Linear behavior is observed for part of 5×10^{-6} Torr at 350°C and at 10^{-5} Torr at 400°C (Fig. 3 and 4). If it is assumed that under these conditions the oxidation rate is controlled by a combination of the rate of impingement of oxygen on the surface and the sticking factor of oxygen on the oxide, a sticking factor of 0.03 at 350°C and 0.025 at 400°C can be calculated.
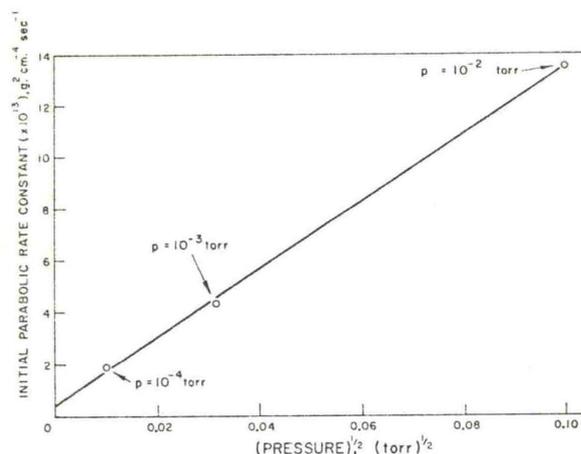

Fig. 11. Initial parabolic rate constant for the oxidation at 350°C and oxygen pressures of 10^{-4}, 10^{-3}, and 10^{-2} Torr plotted against the square root of the pressure.

Activation energies derived from the initial K_p values at 350° and 400°C, and 10^{-4}, 10^{-3}, 10^{-2} Torr are 15, 17, and 22 kcal · mole^{-1}, respectively. The values are obviously not too reliable as oxidation rates were only measured at two temperatures, but they are of some significance. No comparable data for oxidations under similar conditions exists in the literature but higher values of 33 kcal · mole^{-1} (12), for composite oxide formation in the temperature range, 500°-900°C and 45 kcal · mole^{-1} (13) for the growth of magnetite in the range 400°-570°C, are quoted for higher temperature oxidations.

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