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¹ Zachariasen, W. H., *J. Amer. Chem. Soc.*, **54**, 3841 (1932); *J. Chem. Phys.*, **3**, 162 (1935).

² Warren, B. E., *Z. Kristallog.*, **86**, 349 (1933).

³ Warren, B. E., and Biscoe, J., *J. Amer. Ceram. Soc.*, **21**, 49 (1938).

⁴ Robinson, H. A., *J. Phys. Chem. Solids*, **26**, 209 (1965).

⁵ Milligan, W. O., Levy, H. A., and Peterson, S. W., *Phys. Rev.*, **83**, 226 (1951).

⁶ Mackenzie, J. D., and White, J. L., *J. Amer. Ceram. Soc.*, **43**, 170 (1960).

⁷ Zarzycki, J., *Veres et Refractaires*, **11**, 1, 3 (1957).

⁸ Kitchens, T. A., jun., thesis, Rice Univ. (1963).

⁹ Bell, R. J., and Dean, P., *Nat. Phys. Lab. Math. Rep.*, **Ma**, 62 (1967).

CHEMISTRY

Oxidation of Vanadium in the Liquid Oxide Region

At temperatures above the melting point of vanadium pentoxide (675° C), the rate of oxidation of vanadium is extremely rapid and the kinetics have been described¹ in terms of the following equation

$$w - a = kt_m \quad (1)$$

where w is the weight of oxygen absorbed per square cm, t is the duration of oxidation, and a , k and m are constants with m , the rate index, close to 0.7. Although not entirely unknown^{2,3}, such a value is both unusual and difficult to rationalize. It has been considered to be due to a combination of linear and parabolic processes, presupposing similar activation energies unless m is temperature dependent.

The work reported here is an extension of the earlier investigation, with the object of understanding the significance of m . Oxidation experiments were conducted as before¹ using a volumetric apparatus in which vanadium coupons were oxidized under a constant pressure of oxygen at pressures ranging from 100 to 450 torr and temperatures from 690° to 1,050° C. The experiments confirmed the results of the previous study in general; but the rate index m was found to be independent of temperature, and to increase with decreasing oxygen pressure from 0.7 at 450 torr to 0.9 at 100 torr (Fig. 1). Single crystal vanadium⁴ was found to oxidize in a similar manner to polycrystalline material, but the rate constant k was greater.

In view of the exothermic nature of the reaction¹, it was desirable to measure the variation in temperature of

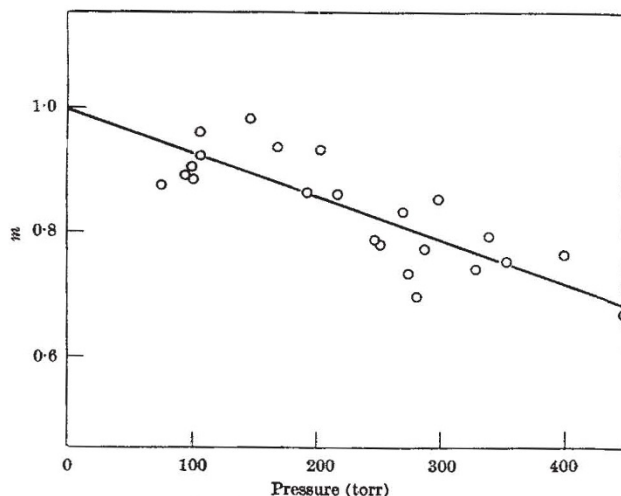


Fig. 1. The rate index " m " plotted as a function of pressure for polycrystalline vanadium.

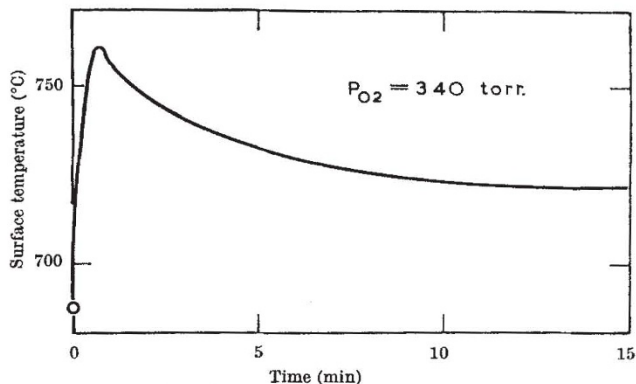


Fig. 2. The variation in temperature of a specimen oxidized at 690° C and 340 torr.

the specimen during the course of the reaction. Accordingly, surface temperature measurements were made using a platinum-platinum/10 per cent rhodium thermocouple in contact with the specimen. This was outside the reaction vessel. The differential signal was recorded on a high speed galvanometer recorder, which was standardized with a potentiometer before and after each run.

Fig. 2 shows the variation in temperature of a specimen oxidized at 690° C, 340 torr; there is an initial temperature rise on admitting oxygen followed by a slow decrease to about 30° C above that of the furnace. At lower pressures the initial temperature rise is less.

That grain boundary effects are not important in determining the form of equation (1) is shown by the fact that single crystal and polycrystalline material behave similarly, and the cause of the unusual value of the rate index m must be sought elsewhere. A layer of liquid oxide remains on the metal surface throughout the reaction, and we think that the rate of oxidation is controlled by diffusion through this layer; for a layer of constant thickness, linear kinetics are to be expected. This, however, is only valid for isothermal conditions, whereas in fact the specimen temperature varies considerably. During the early stages the rate of reaction will be relatively high and will decrease as the temperature falls; so that the overall reaction rate will decrease with time ($m < 1$). At lower pressures the initial temperature rise is less and there is little difference in initial and final rates so that m is close to unity.

Calculations indicate that the rate of change of temperature is compatible with this interpretation. The actual increase in temperature, however, is less than that calculated; this may be due to the difficulty of ensuring that the measuring couple is at the true interface temperature.

The non-linearity of the rate equation is thus a consequence of the non-isothermal nature of the reaction and does not represent a steady state reaction mechanism.

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¹ Price, W. R., and Stringer, J., *J. Less Common Metals*, **8**, 165 (1965).

² Stringer, J., *J. Less Common Metals*, **6**, 207 (1964).

³ Gebhardt, E., and Seghezzi, H. D., *Z. Metallkunde*, **50**, 248 (1959).