

Table 1

Metal	Value of n (rate-law)	Temperature increase	Temperature region	Activa- tion energy
Titanium	$n = 1$ (parab.)	3.86 deg. C./min.	700–900° C.	53 kcal.
Nickel	$n = 1$ (parab.)	2.23 deg. C./min.	700–1,050° C.	41 kcal.
Zirconium	$n = 2$ (cubic)	3.86 deg. C./min.	700–1,050° C.	45 kcal.
Copper	$n = 1$ (parab.)	2.23 deg. C./min.	750–1,000° C.	35 kcal.

The method described has been tested for nickel, zirconium, copper and titanium over the temperature range 400–1,050° C., and the results are shown in Table 1.

The activation energies observed are all in good agreement with previously published values² obtained by the conventional method of plotting $\ln k$ versus $1/T$. The value for titanium was checked in this laboratory by the conventional method which gave an activation energy of 52 kcal. in the parabolic rate-law region. Furthermore, the method gave good estimates of the temperature regions in which different rate-laws are observed. In the case of oxidation of titanium³, which follows a cubic rate-law in the temperature region 400–600° C., a parabolic rate-law between 600° and 900° C., and a linear rate-law above approximately 900° C., the method gave results which were in agreement with conventional studies. Results for the oxidation of nickel are shown in Fig. 1.

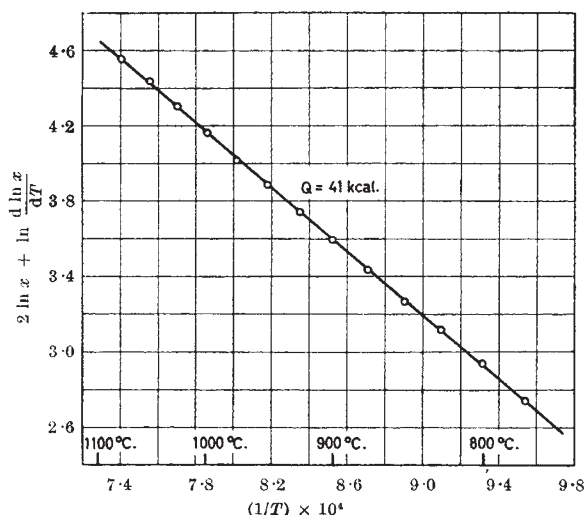


Fig. 1. Determination of the activation of oxidation of nickel by oxidizing under conditions of linearly increasing temperature

A detailed account of the method and the results for a number of metals and alloys will be published elsewhere.

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¹ Baur, J. P., Bridges, D. W., and Fassel, jun., W. M., *J. Electrochem. Soc.*, **102**, 490 (1955).

² See Kubaschewski, O., and Hopkins, B. E., "Oxidation of Metals and Alloys" (London, 1953). See Hauffe, K., "Oxydation von Metallen und Metallegierungen" (Springer Verlag, Berlin, 1956). Belle, J., and Mallet, M. W., *J. Electrochem. Soc.*, **10**, 339 (1954).

³ Kofstad, P., and Hauffe, K., *Werkstoffe und Korrosion*, **7**, 642 (1956).

Preparation of Maghæmite by Electrolysis

WHEN nitrate solutions are employed as the catholyte in an electrolytic cell, with the electrodes separated by an anion-permeable ion-exchange membrane, many metallic hydroxides tend to precipitate in the cathode compartment, to compensate for the loss of nitrate ions to the anolyte. For a trivalent cation, the overall reaction can be represented as follows:



With ferric nitrate as catholyte, however, the first-formed precipitate is dark brown, magnetic and contains only 3–4 per cent of water after drying at room temperature. On ignition at temperatures above 500° C., the product is rapidly converted to red, non-magnetic ferric oxide, in contrast to the mineral magnetite (Fe_3O_4), which retains its magnetism after similar treatment. The air-dried material contains a variable proportion of ferrous iron which is, on the average, ten times less than that expected from magnetite. The precipitate thus exhibits the same properties as maghæmite, which is closely related to synthetic gamma- Fe_2O_3 .

It is surprising to find that an oxide of iron containing so little water can be prepared from aqueous solutions at room temperature. The majority of methods¹ for the preparation of gamma- Fe_2O_3 rely on the preliminary formation of the monohydrate (10.1 per cent water), with subsequent dehydration to the anhydrous magnetic oxide at 230–260° C. Good yields of maghæmite can be obtained by the electrolytic procedure, however, provided that the catholyte pH is maintained in the range 1.0–2.5. At higher pH values, ordinary ferric hydroxide (25.2 per cent water) is the main constituent of the precipitate.

We have also shown that ammonia, formed by cathodic reduction of nitrate, is not inimical to the formation of maghæmite and that the nature of the cathode (whether platinum or graphite) is not a critical factor.

Independent confirmation of the identity of the material has been obtained through the courtesy of Dr. A. D. Wadsley, of this Division, who has shown that the somewhat diffuse X-ray powder diffraction patterns can be indexed in terms of a primitive cubic lattice, the cell edge $a = 8.35 \pm 0.02$ Å. falling within the range of maghæmite or gamma- Fe_2O_3 . The patterns appear to be derived from a superlattice of the spinel grouping. While we make no claims that this superlattice may be caused by the systematic incorporation of water molecules or protons, it is of interest that the chemical composition of our material is not far removed from the formula HFe_3O_8 (2.2 per cent water), which is in good agreement with an earlier report² on superstructures in spinels.

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¹ See, for example, Brit. Pat. 640,438. Booth, H. S., "Inorganic Syntheses", **1**, 186 (McGraw-Hill, New York, 1939).

² Braun, P. B., *Nature*, **170**, 1123 (1952).