Letters to the Editor.

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The Structure of Catalytically Active Copper.

THE nature of the change that occurs on the activation of a metallic catalyst by alternate oxidation and reduction, or by continued use, and the change that occurs during sintering, has been an open question (cf. *Proc. Roy. Soc.*, A, vol. 107, p. 277 ; vol. 110, p. 283). The solution of this problem
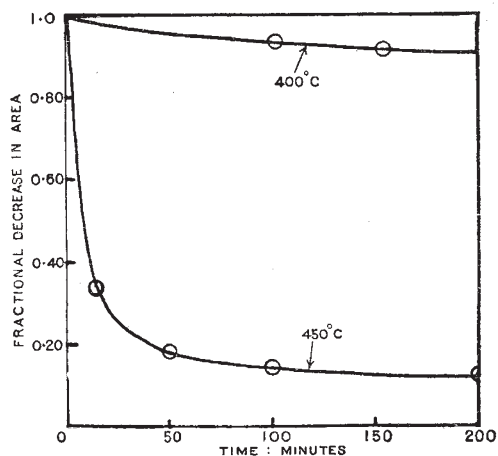
FIG. 1.

definitely would go far towards establishing the theory of centres of activity on an indisputable foundation, since it is necessary to show that both the area and the nature of the surface change (cf. the discussion by Hinshelwood, " Kinetics of Chemical Change in Gaseous Systems," Clarendon Press, p. 194).

Now the observations of Dunn (*Proc. Roy. Soc.*, A, vol. 111, p. 210) on the use of interference colours, in following quantitatively the growth of the oxide film on copper, give a method of estimating the linear rate of growth of the oxide covering the individual grain compared with that on 'inactive copper.' Palmer (*Proc. Roy. Soc.*, A, vol. 103, p. 444) showed that the conductivity of a mixed copper-copper oxide film was directly proportional to the copper content of the supported film ; thus the rate of fall of the conductivity of the film is a measure of the mass of copper being oxidised in unit time, and a method is available for estimating the massive rate of growth of the oxide compared with that on 'inactive copper.'

Let a be the thickness of the oxide film, S represent the area of surface, and C be the electrical conductivity of the mixture of oxide and metal. Let the suffix 1 denote the values of these quantities for an activated or sintered catalyst, at time t after the commencement of the oxidation at constant temperature ; and the suffix 2 represent the same variables either for the film before activation, or for the fully activated film before annealing.

Then

$$\frac{\left(\frac{da}{dt}\right)_1 \cdot S_1}{\left(\frac{da}{dt}\right)_2 \cdot S_2} = \frac{\left(\frac{dC}{dt}\right)_1}{\left(\frac{dC}{dt}\right)_2}. \quad \ldots \quad (1)$$

Thus S_1/S_2 can be evaluated, and we have a method of measuring the increase of area on activation, and the decrease of area on sintering.

The observations for the activation of a catalyst present experimental difficulties, owing to the irregular nature of the first reduction and oxidation in many cases ; but they are of great theoretical interest and, so far, seem to indicate that the increase in area of the supported copper films on successive reduction is not large. The nature of the surface alters considerably, since the linear rate of oxidation increases markedly.

In the case of sintering, the observations can be made with accuracy ; the nature of the surface is changed since the linear rate of oxidation falls, and the increase in surface area is marked. Continued exposure to high temperature does not cause the area to diminish indefinitely, but a definite limit is reached corresponding to each temperature. The effect of annealing a supported copper film at 450° C. and 400° C. is shown in the accompanying diagram (Fig. 1), the results being worked out by the method previously described.

The relative rate of increase of thickness of the oxide film slows down very considerably, as the time of sintering is increased. Dunn's conclusions (*loc. cit.*) that " the structure of a metal may be brought out owing to the variation of the oxidation rate of different crystal faces," and that " For a definite time of oxidation each crystal face will be characterised by a different colour," seem to provide indisputable evidence that, as well as the area change that occurs during activation and sintering, there is also an unmistakable change in the nature of the surface.

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Magnetic Properties of Single Crystals of Nickel.

THE magnetic properties of single crystals of iron have been examined by Webster (*Proc. Roy. Soc.*, **107**, p. 497, and **109**, p. 570), Honda, Kaya, and Masuyama (NATURE, May 29, 1926), and more recently Gerlach (*Zeit. für. Phys.*, **38**, p. 828, 1926). Considerable differences have been shown to exist between the

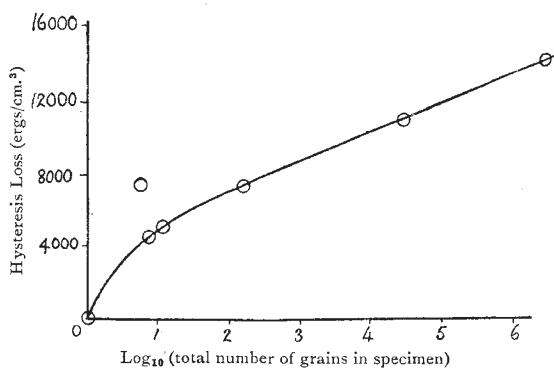FIG. 1

magnetic properties of the polycrystalline metal and the single crystal.

We have recently succeeded in preparing crystals of nickel of several cubic centimetres in volume, from which specimens large enough for magnetic measurements can be obtained. The present note contains an account of a preliminary investigation on the variation of hysteresis loss with grain size. The specimens used were cylindrical rods of 20 mm. by 2 mm. diameter. The hysteresis loss, as in the case