

the evidence for the existence of a potential for the diurnal magnetic variations appears to us adequate. The onus of proof to the contrary seems to rest with any who may controvert the conclusion, and the most direct evidence that could be brought forward would consist of calculations of line-integrals such as are here given, but based on more accurate data: these would require to be specially obtained for the purpose. The undertaking would be difficult and costly unless new and simpler recording devices than those now in use should become available.

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*A New Interference Method of measuring the Surface Area of Film Catalysts. Part I.—The Theory.*

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One of the great difficulties presented in all investigations on the catalysis of heterogeneous gas reactions is the experimental preparation of a catalyst of definite mass associated with a measurable and reproducible surface area. Masses of metallic oxide, when reduced at low temperatures, give a metal which has often a considerable activity, but an entirely unknown surface area, which is liable to considerable variation. The use of supported catalysts is a considerable advance. The mass of the catalyst is fixed, and since the whole mass may be rapidly oxidised and reduced, leaving no massive metal beneath unattacked, the variations in the surface area presented to the gas phase is considerably restricted. The external surface will vary with the method of production of the film, and it is the purpose of this paper to describe a general method of measuring this surface, the determination of the surface area of these films being of vital importance in the study of their catalytic properties.

*On the Meaning which may be assigned to the Surface Area of a Catalyst.*

The area of a continuous bounded surface which is perfectly plane does not vary with the means of measurement adopted. When, however, irregularities are present in the surface, the surface may be considerably increased, the increase varying both with the magnitude of the irregularities and the means

of estimation adopted. By some methods of measurement the irregularities are disregarded, by others they are included.

The measurement of length involves the same problem. A vessel sailing round the coast of England keeping within a few miles of the shore would travel a much smaller distance than would a man walking round the edge of the cliffs, and the man would travel less far than an insect making the same tour.

The smallest area that could be ascribed to the film is that of the inert support; the largest value for chemical purposes is the area of a surface composed of hydrogen atoms, all in contact with each other, and with the catalyst surface, which is thus completely covered.\* There is grave doubt whether this maximum value could be obtained experimentally, for not only is there a pronounced lack of heterogeneity in the adsorbing power of a reduced metal for hydrogen, but the problem is also complicated by the solution of the gas in the metal.

The evidence shows that adsorption methods can only hope to measure a fraction of the true surface.

To make certain that the surface is covered with a homogeneous film one is driven to chemical methods of attacking the surface, since then it may sometimes be asserted that the whole surface is covered with a homogeneous film. If the mass of this film be measured ( $w = \rho \cdot x \cdot S$ ), and the thickness  $x$  be independently estimated, then the value of  $S$  can be obtained if the density of the film be known.

When a gas reacts with a solid surface, and the specific volume of the product is greater than that of the original metal, then the surface becomes wholly covered with the reaction product, and, further, the rate of reaction is chiefly regulated by the rate of diffusion of the gaseous reactant through the film already present. These conditions lead to the production of very uniform films over a metallic surface.

A considerable amount of experimental investigation† has been made on the

\* It seems possible that some method of electrodeposition of hydrogen from solution might be adapted to measure this area, but the difficulty is to obtain satisfactory evidence that the quantity of electricity passed has actually caused the production of a complete and unimolecular film of hydrogen over the surface.

† Joannis, 'C. R.,' vol. 158, p. 1801 (1914); Berger, *ibid.*, pp. 1502, 1798; Stahl, 'J. Soc. Chem. Ind.,' vol. 23, p. 1158 (1914); Tammann, 'Z. Anorg. Chem.,' vol. 111, p. 78 (1920); Tammann and Koster, *ibid.*, vol. 123, p. 196 (1922); Hinshelwood, 'Roy. Soc. Proc.,' A, vol. 102, p. 318 (1922); Palmer, 'Roy. Soc. Proc.,' A, vol. 103, p. 444 (1923); Evans, 'J. Chem. Soc.,' vol. 127, p. 2484 (1925), and 'Roy. Soc. Proc.,' A, vol. 107, p. 228 (1925); Dunn, 'Roy. Soc. Proc.,' A, vol. 111, p. 210 (1926); Pilling and Bedworth, 'J. Inst. Metals,' vol. 29, p. 529 (1923); Constable, 'Roy. Soc. Proc.,' vol. 107, p. 270 (1925), vol. 115,

oxidation and reduction of metallic copper. During oxidation the surface is covered with a continuous film of oxide, which under some conditions shows interference colours. Direct spectrophotometric measurements of the intensity and wave-length of the light reflected from oxidised surfaces of iron, nickel and copper leave no doubt that interference is the main cause of production of the colour sequences;\* and thus the colour of these films uniquely determines their thickness when the order of the colour and the refractive index of the film is known. We have therefore the means of developing a general method of evaluating the surface area.

*Methods of using Interference Films to Determine Surface Area of Metallic Film Catalysts.*

Let  $S$  be the surface area of metal of mass  $M$ , forming  $W$  grams of compound when completely converted by the gaseous reagent.

$w$  be the mass of the film covering the metal at time  $t$ .

$g$  be the thickness of a film of air showing the same colour.

$\mu$  be the refractive index of the oxide for wave-length  $\lambda$ .

$C$  be the electrical conductivity of the metallic film when partially attacked, and

$C_0$  be the initial conductivity.

$\lambda$  be the wave-length of the absorption or reflection maximum in the spectrum of the reflected light.

I.—Direct measurement of  $S$  from measurements of  $w$  and spectrophotometric observations on the light reflected from the coloured film.

The thickness of the film  $x = (2n - 1)\lambda/4\mu$ ;  $n = 1, 2, 3, \dots$ , etc., and  $\lambda$  is the wave-length of the absorption band, or  $x = n\lambda/2\mu$ ;  $n = 1, 2, 3, \dots$ , when there is a maximum of reflection.

Hence  $w = S \cdot \rho \cdot (2n - 1)\lambda/4\mu$  or  $S\rho n/2\mu$ ; thus, on plotting  $w$  against  $n'\lambda/\mu$ ,† a straight line is obtained from which the area  $S$  is determined.  $S/M$  is found by a separate determination of  $M$ .

p. 570 (1927), vol. 117, p. 376 (1928), and 'J. Chem. Soc.', vol. 127, p. 1578 (1927), and 'Nature,' vol. 118, p. 730 (1926), vol. 119, p. 349 (1927), vol. 120, p. 769 (1927). The fact that reduction of the oxide only occurs at the metal oxide interface is well brought out by Pease and Taylor, 'J. Amer. Chem. Soc.', vol. 43, p. 2179 (1922); Jones and Taylor, 'J. Phys. Chem.', vol. 27, p. 623 (1923).

\* 'Roy. Soc. Proc.,' A, vol. 117, p. 376 (1928), and vol. 115, p. 570 (1927).

†  $n'$  represents the required integer.

II.—From data on the spectrophotometric analysis of the reflected light and the conductivity of the film.

The fall in conductivity is taken as a measure of the amount of the metallic film that is converted into the covering film, therefore

$$\frac{C_0 - C}{C} = \frac{w \cdot p}{M} = \frac{S \rho p \lambda}{M} \cdot \frac{2n - 1}{4\mu} \quad \text{or} \quad \frac{S \rho p \lambda}{M} \cdot \frac{n}{2\mu},$$

where  $p$  is the percentage of metal in the covering film. Hence, writing  $\Delta c$  for the fall in conductivity we have

$$\frac{S}{M} = \frac{\Delta c \cdot p}{\rho \cdot C} \cdot \frac{(2n - 1) \lambda}{4\mu}$$

for the absorption bands and

$$\frac{\Delta c \cdot p}{\rho C} \cdot \frac{n \lambda}{2\mu}$$

for the reflection bands. It is convenient to plot  $\Delta c/C$  against  $n' \lambda/\mu$ , the slope of the line determining  $S/M$ .

III.—From observation of the surface colour expressed in terms of the equivalent air thickness of the covering film and the mass of the film.

The mass of the covering film may be expressed as

$$w = S \cdot \rho \cdot q/\mu.$$

Thus  $S = \mu \cdot w/\rho \cdot q$ , and if a separate determination of  $M$  be made, the value  $S/M$  is determined.

IV.—From simultaneous observations of the surface colour and the electrical conductivity of the metallic film.

We have

$$\Delta c/C = w \cdot p/M,*$$

whence

$$\Delta c/C = p \cdot \rho \cdot q \cdot S/\mu M,$$

or

$$S/M = \Delta c \mu / C \cdot q \cdot \rho \cdot p.$$

It is convenient to plot  $q/\mu$  against  $\Delta c/C \rho p$ , the straight line slope enabling  $S/M$  to be measured.

\* It is to be observed that  $p$ , being the percentage of metal in the metallic oxide, is altered only slightly by uncertainty in the nature of the oxide formed. Thus, if the composition of the surface film is only approximately known, the method is still tolerably accurate. The refractive index can be found by reflecting polarised light from the film.

V.—From the initial values of the oxidation constants determined from observations of the surface colours, together with the mass of oxide produced, or the change in conductivity of the metallic film.

Pilling and Bedworth, and Dunn (*loc. cit.*), have found that  $w^2 = kt$ , where  $w$  is the total mass of oxide formed, is an approximation to the law of formation of the film obeyed with fair accuracy by the sintered metal but showing very distinct fall in the value of the constant  $k$  for the activated metal. The law is useful in enabling the initial value of  $k$  to be extrapolated.

Thus

$$2w \frac{dw}{dt} = k_w$$

hence

$$\frac{dw}{dt} = \frac{k_w}{2w} = \frac{1}{2} \sqrt{\frac{k_w}{t}}$$

Similarly

$$\frac{dq}{dt} = \frac{1}{2} \sqrt{\frac{k_q}{t}}; \quad \frac{dx}{dt} = \frac{1}{2} \sqrt{\frac{k_x}{t}},$$

and

$$2(C_0 - C) \frac{dC}{dt} = k_c,$$

therefore

$$\frac{dC}{dt} = \frac{1}{2} \sqrt{\frac{k_c}{t}}$$

The rate of formation of the layer as a fraction of the total amount of oxidised film possible

$$\frac{e_M}{e_0} \frac{\rho S}{\mu M} \frac{dq}{dt} = \frac{1}{C_0} \frac{dC}{dt}$$

is equal to the rate of disappearance of the metal expressed similarly. Thus

$$\frac{S}{M} = \frac{e_0}{e_M} \cdot \frac{\mu}{\rho C_0} \sqrt{\frac{k_c}{k_q}},$$

where  $e_0$  and  $e_M$  are the equivalent weights of the metal and oxide respectively.

If  $w$  be measured the relation

$$\frac{\rho \cdot S \cdot dq}{\mu dt} = \frac{dw}{dt}$$

becomes

$$S = \frac{\mu}{\rho} \sqrt{\frac{k_w}{k_q}},$$

and an outside measurement of  $M$  has to be made.

VI.—Comparative values of  $S_1/S_2$  may be obtained when the nature and the refractive index of the film are uncertain.

For

$$\frac{\left(\frac{dq}{dt}\right)_1 \cdot S_1}{\left(\frac{dq}{dt}\right)_2 \cdot S_2} = \frac{\left(\frac{dC}{dt}\right)_1}{\left(\frac{dC}{dt}\right)_2},$$

whence

$$\frac{S_1}{S_2} = \frac{\left(\frac{dC}{dt}\right)_1 \cdot \left(\frac{dq}{dt}\right)_2}{\left(\frac{dC}{dt}\right)_2 \cdot \left(\frac{dq}{dt}\right)_1},$$

and no value of  $p$  or  $\mu$  is assumed.

*Reasons for the Introduction of the New Method.*

The hot-wire technique, introduced by Hinshelwood, enables gas reactions proceeding at high temperatures to be studied in a closed vessel surrounded with melting ice. Pressure measurements are sufficient to describe the changes taking place in the vessel. Many useful data have been obtained by Hinshelwood and his co-workers by the use of this method.

The nature of the surface presented by the wire is a very uncertain factor, and so the wire has been replaced by a continuous, but very thin metallic film supported by china clay. This film has been obtained by electrodeposition by a method which is described in the following paper, and its mass is accurately known. It may be heated to any desired temperature by the passage of an electric current through the film, and the treatment to which the surface is subjected can be varied at will. At the same time the methods previously described enable the visible surface to be measured.

The catalyst is therefore standardised in a way which has not been possible previously. It is the purpose of this series of papers to apply the method of measurement to a whole series of metallic films.