186. *The Oxidation of Calcium in Moist Oxygen.*

By S. J. GREGG and W. B. JEPSON.

The oxidation of calcium in moist oxygen corresponding to saturation with water at 0° and 25° has been studied by a thermal-balance technique at temperatures in the ranges 200—400° and 50—525°, respectively. It is shown that the reaction is between calcium and water vapour, the oxygen acting as a carrier gas; at temperatures above 200° the reaction is $Ca + H_2O = CaO + H_2$, followed by $CaO + H_2O = Ca(OH)_2$ when all the metal has been oxidised. The product formed below 200° is white, whereas that formed at the higher temperatures is green. This coloration is ascribed to the presence of calcium hydride.

The rate of oxidation is shown to *decrease* with increasing temperature over the ranges 50—150°, 250—300°, and 425—525°, and to increase with increasing temperature in the ranges 200—250° and 325—375°. At 425° and above, " breakaway " occurs. The kinetic results are in broad accord with those of other workers for the oxidation of calcium in water vapour.

The reaction mechanism is discussed.

THE kinetics of the oxidation of calcium in dry oxygen was the subject of a recent paper[1] (hereafter referred to as Part I), and in the present paper the study has been extended to moist oxygen, a field which has hitherto received but little attention. The ranges 200—400° and 50—525° have been investigated with oxygen saturated with water vapour at 0° and 25°, respectively.

The results obtained indicate that the reaction occurs with the water vapour alone, the oxygen merely acting as a carrier gas.

EXPERIMENTAL

Materials.—The calcium (stated to be 99·95% pure, excluding magnesium the content of which was 0·5% maximum) was part of the same batch as was used in the earlier paper,[1] and the surface was again prepared by filing.

Method.—The weight gain of the sample as a function of time was determined gravimetrically by means of a thermal balance.[2] Two humidities of oxygen were used, corresponding to saturation with water vapour at 25° (mixture A) and at 0° (mixture B), the saturation pressures being 23·8 and 4·58 mm., respectively. One set of experiments was carried out with argon in place of oxygen, and a water content corresponding to saturation at 25° (mixture C, 23·8 mm. saturation pressure).

Results.—(a) *Kinetics.* The curves for mixture A at temperatures in the range 50—525° are given in Figs. 1—4. They clearly do not conform to a simple pattern, and the gain of weight after a given time does not increase uniformly with increase in temperature, but actually decreases between 50° and 150° (Fig. 1), between 250° and 300° (Fig. 2), and between 425° and 525° (Fig. 4). The curves fall into three groups: (i) where the rate of oxidation continuously decreases along branch OA (cf. 50°, Fig. 1) to reach a constant or nearly constant rate along AB; (ii) where the rate *increases* along OA (cf. 250°, Fig. 2) to a constant rate along AB; (iii) where the rate first decreases until at P (cf. 425°, Fig. 4) it increases fairly rapidly in the manner characteristic of " breakaway." The Table summarises the type of curve and the average linear rate for each temperature; it will be noted that at 425° and above, the curves are exclusively of Group (iii). The linear rate of Groups (i) and (ii) in duplicate runs at a given temperature agreed within ±10%; in the Group (iii) the weight gains at a given temperature again agreed within ±10%, except at 525° where the onset of breakaway varied, in different runs, between 6 and 20 hr. (Fig. 4).

Although a linear branch, corresponding to a constant rate of oxidation, was a characteristic feature of the curves of Groups (i) and (ii), it does not follow that the metal would

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[1] Gregg and Jepson, *J.*, 1960, 712.

[2] Gregg and Jepson, *J. Inst. Metals*, 1958—59, **87**, 187.

FIG. 1. *Oxidation of calcium in moist oxygen (mixture A) at* 50—150°. (*Curve OD is calculated from the data of Svec and Apel*[6] *and is referred to in the text.*)

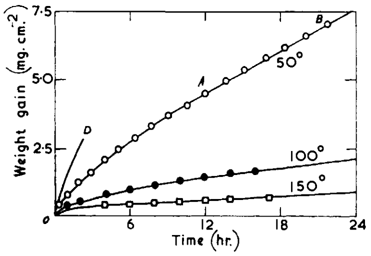


FIG. 2. *Oxidation of calcium in moist oxygen (mixture A) at* 150—375°.

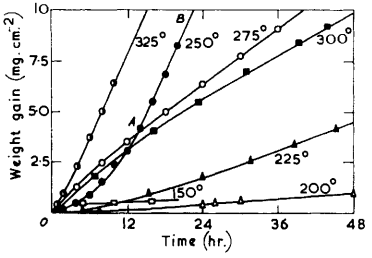


FIG. 3. *Oxidation of calcium in moist oxygen (mixture A) at* 325—400°.

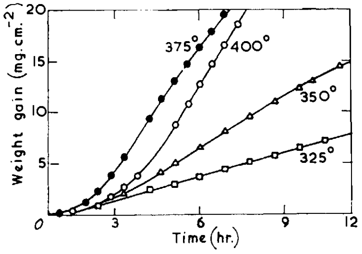


FIG. 4. *Oxidation of calcium in moist oxygen (mixture A) at* 400—

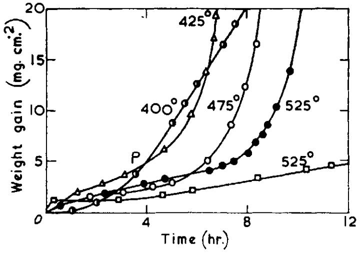


FIG. 5. *Oxidation of calcium in moist oxygen (mixture A) at* 250—250°. *The weight gain is now plotted as the specific weight gain* (*g./g. of initial metal*) *and not as mg./cm.*^{2} *as in Figs.* 1—4. *The curves for* 300° *and* 350° *accidentally coincide: the initial area of metal was not the same in each run. The specific weight gains corresponding to conversion into oxide and into hydroxide are* 0·4 *and* 0·85 *g./g., respectively.*

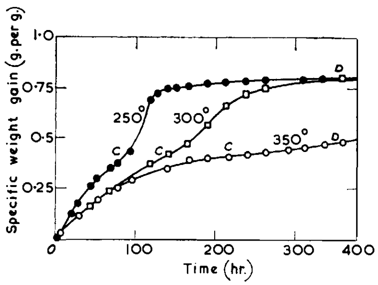
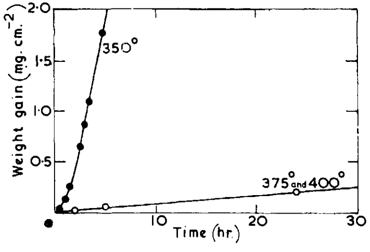


FIG. 6. *Oxidation of calcium in moist oxygen (mixture B) at* 350—400°.



continue to oxidise to completion at this rate. Thus in the 400-hr. runs at 250°, 300°, and 350° (Fig. 5) the linear branch ended at about 20 hr. and was succeeded by a curve of variable slope.

In mixture B the experiments were confined to the temperature range 200—500°. For temperatures up to and including 350° the curves closely resembled those for mixture A except that the linear rate was smaller (Table); but at 375° and 400° there were marked differences between the two mixtures; the results for these two temperatures now fell on the *same* curve, which lay much below that for 350° (contrast Figs. 6 and 3).

Runs carried out at six representative temperatures between 50° and 425°, with argon in place of oxygen (mixture C), gave curves agreeing within experimental error with those obtained by using the oxygen mixture of the same humidity (mixture A) at the same temperatures, and the appearance of the samples at the end of the run was similar; moreover, in a blank test using dry argon alone at 525°, the weight gain in 24 hr. was only 0·25 mg./cm.^{2}. It seems clear, therefore, that the oxygen functions merely as a carrier gas.

(b) *Reaction product.* At all temperatures the reaction product remained adherent to the metal during the run itself, but fragments of it spalled on cooling from heavily oxidised specimens. The specific surface areas of the products prepared at 50°, 100°, and 350°, as measured by the method of krypton sorption,[4] were 41, 18, and >100 m.^{2} g.$^{-1}$, respectively.

With all three mixtures the colour of the product varied according to the temperature of the experiment: at 50° it was a white layer (hydroxide), and 100° and 150° it was light grey with traces of white; at 200° and above it had a colour which varied from dark green at 250° to khaki at 350°; and at 425° and above it was straw-coloured with patches of green.

Now, in Part I, the oxide obtained in dry oxygen also had a green colour which was assumed to be due to the excess of calcium thought to be present. It seems reasonable, however, to suppose that the constituent responsible for the colour is common to oxides prepared both in dry and in moist oxygen; and it is now suggested that this constituent is calcium hydride. The presence of this substance has already been demonstrated [3] in the product from calcium oxidised in pure water vapour at 177—369°; and its content was determined [1] directly in the products obtained at 300° and above (Table) by chipping off samples of the oxide and measuring the volume of hydrogen evolved on treatment with water. The source of the hydride present in the product formed in dry oxygen could be hydrogen dissolved in the metal.

Sections of a number of samples which had been oxidised at 300—350° indicated that the metal was completely oxidised as soon as the specific weight gain reached 0·40 g. per g., which is the calculated value for the completion of the reaction

$$\mathrm{Ca} + \mathrm{H_2O} = \mathrm{CaO} + \mathrm{H_2} \qquad (1)$$

It seems clear, therefore, that branch *OC* of the curves in Fig. 5 corresponds to reaction (1) which is complete at *C*, and branch *CD* to the hydration of the oxide

$$\mathrm{CaO} + \mathrm{H_2O} = \mathrm{Ca(OH)_2} \qquad (2)$$

which did not, however, proceed to completion (*i.e.*, specific weight gain of 0·85 g. per g.) in the time of the experiments. Associated with this hydration is the reaction of the calcium hydride with water vapour, for the green colour of the oxide was found to persist only so long as some metal remained unoxidised: thus, samples oxidised at 350° to a specific weight gain of 0·45 appeared white although sections revealed some green coloration within the sample.

Samples oxidised in mixture B were similar in appearance to those oxidised in mixture A, except that the oxide was paler for a given temperature. It was not possible to obtain sufficient oxide for a determination of the calcium hydride content.

DISCUSSION

Taken as a whole, the results are surprisingly complex; the curves show a variety of form and there are three ranges in which the rate of oxidation decreases with increase in temperature, *viz.*, 50—150°, 250—300°, and 425—525°. Although it is not uncommon in studies of the oxidation of metals to encounter a single range of temperature over which

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[3] Gibbs and Svec, *J. Amer. Chem. Soc.*, 1953, **75**, 6053.

[4] Smith, Ph.D. Thesis, Exeter, 1958.

the reaction rate has a negative temperature coefficient,[1,5,6] yet it is unusual to find three such temperature ranges with one metal, as in the present system.

Although some fairly definite conclusions can be drawn as to the nature of the overall reaction at most of the temperatures, it is not yet possible to explain the curves in detail. One can do little more than indicate the kind of factors involved and suggest how they might influence the reactions.

The present results establish that when calcium is oxidised in moist oxygen, only the water vapour reacts and the oxygen thus functions as an inert carrier gas. Svec and Apel[6] (Fig. 1, curve *OD*) have already shown that, at temperatures in the range 20—70°, calcium reacts with water vapour according to

$$Ca + 2H_2O = Ca(OH)_2 + H_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

and in view of the similarity both in the form of the curves and in the appearance of the samples for 50°, 100°, and 150°, there is little doubt that equation (3) also represents the reaction at 100° and 150°.

At temperatures in the range 250—350°, on the other hand, no calcium hydroxide appears in the product until all the calcium has been consumed; conversion into hydroxide then begins, and proceeds at a rate which decreases with increase in temperature (Fig. 5). The reaction sequence is thus (1) followed by (2). At temperatures above that at which the dissociation pressure of calcium hydroxide exceeds the partial pressure of water vapour in the mixture (373° for mixture A [7]), the hydration stage (2) will be absent and the product will be oxide, with possibly a monolayer of chemisorbed water on its surface.

Calcium hydride was not the main product at any temperature, its content never exceeding second-order proportions (Table). This is in contrast with Gibbs and Svec's conclusion[3] that, in water vapour at 23·8 mm. and at temperatures in the range 177—369° (later amended to 330—400° [8]), the reaction is exclusively

$$2Ca + H_2O = CaO + CaH_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

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Temp.	Type of curve	Linear rate (mg./cm.^{2}/hr.)		CaH_2 content of scale formed in mixture A (mg./g.)
		Mixture A	Mixture B	
50°	I	0·248	—	—
100	I	0·068	—	—
150	I	0·022	—	—
200	II	—	—	—
225	II	0·129	0·045	—
250	II	0·687	0·200	—
275	I	0·213	0·050	—
300	I	0·166	0·065	8·8
325°	II	0·673	—	8·2
350	II	1·78	0·73	—
375	II	(3·89)	—	7·1
400	II	(4·11)	—	6·9
425	III	—	—	4·4
475	III	—	—	1·1$_9$
525	III	—	—	1·0$_1$

as long as any calcium remains unoxidised. In the present study, one run at 350° was stopped when the weight gain was that corresponding to completion of reaction (4), *viz.*, 0·23 g. per g., yet an appreciable amount of unconsumed metal could be seen in the sectioned sample.

Attempts to fit equations to the curves were unsuccessful; this was true even at 50°, which lies within the range of temperatures (20—70°) where, according to Svec and Apel,[6] the logarithmic law

$$w = k \log (1 + ct) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

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[5] Bridges and Fassell, *J. Electrochem. Soc.*, 1956, **103**, 326; Aylmore, Gregg, and Jepson, *ibid.*, 1960, **107**, 495; Hopkinson, *ibid.*, 1959, **106**, 102.

[6] Svec and Apel, *J. Electrochem. Soc.*, 1957, **104**, 346.

[7] Tamaru and Siomi, *Z. phys. Chem.*, 1932, *A*, **161**, 421.

[8] Svec and Staley, *J. Electrochem. Soc.*, 1958, **105**, 121.

holds for calcium in water vapour (w is the weight gain at time t, and k and c are constants). It is interesting that these workers also found a negative temperature coefficient for k with an "energy of activation" (calculated from the Arrhenius plot) of $-7{\cdot}5$ kcal. mole^{-1} as compared with $-6{\cdot}6$ kcal. mole^{-1} calculated from the linear rates at 50°, 100°, and 150° of the Table.

The relatively high values of the specific surface of the product show it to be porous to water vapour; the conventional picture[2] of an oxide scale which cracks and becomes porous to the gaseous reactant, leaving a thin film (barrier film) adhering to the metal, therefore seems applicable. The reaction then proceeds by diffusion of Ca^{2+} ions and their electrons across this film to meet the water adsorbed at its outer surface (Fig. 7).

The overall rate of reaction at any one temperature will then be determined by the slowest of the following three processes: (1) the diffusion of Ca^{2+} ions across the barrier film; (2) the adsorption (physical or chemical) of water molecules at the film–gas interface; (3) the reaction between Ca^{2+} ions and water at the film–gas interface. With regard to process (1), the rate of diffusion of Ca^{2+} ions across the barrier film will depend upon two factors: (i) the thickness of the film itself (the thinner the film, the greater the rate of diffusion) which will depend upon the rate of cracking;[2] (ii) the concentration of imperfections in the barrier film. These imperfections could arise from the dissolution of impurities from the metal in the oxide and also from the presence of hydroxyl and carbonate ions in an oxide lattice or of oxide and hydroxyl ions in a carbonate lattice. (The freshly prepared metal surface rapidly tarnishes in air.)

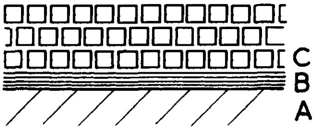

FIG. 7. *Showing the cross-section of specimen during non-protective oxidation.* (A) *Metallic calcium;* (B) *barrier film of oxide or hydroxide;* (C) *porous, outer scale.*

Now each of the processes (1), (2), and (3) will have its own temperature coefficient and each of the factors (i) and (ii) will separately depend upon temperature; and it is clear, therefore, that the kinetics of the overall reaction could vary in a complex manner with temperature. In the absence of further data, however, it does not seem possible to provide a more detailed explanation of the experimental dependence of kinetics on temperature.

There was one rather curious feature of the results: the oxide fails to hydrate until all the metal has been consumed, despite the fact that the scale is exposed to water vapour and is highly porous. The water molecules must therefore proceed preferentially to the film–gas interface rather than to the oxide–hydroxide interface. Presumably the water molecules migrate over the surface of the oxide particles composing the scale to reach the surface of the barrier film where they react; a concentration gradient of adsorbed water molecules is thus set up and persists so long as calcium remains. If the rate of migration and of reaction is greater than the rate of hydration, the facts are explained.

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THE UNIVERSITY, EXETER.

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