

ally small, often according to some fractional power². During an investigation of the oxidation of aluminium alloys in high-temperature steam we have found a very much greater dependence on pressure.

In our experiments, the alloy "Aereal 1" (aluminium + 2.5 wt. per cent nickel), chosen for study because of its good resistance to high-temperature water³, was exposed to dry steam at 325°C. and pressures from 550 to 1,500 lb./in.² for periods up to 160 hr. Oxidation was assessed by the gain in weight of the specimen—a valid measure, since wholly adherent films were formed. Oxidation/time curves for each pressure followed a parabolic equation ($w = Kt^m$), where $m = 0.48$. The constant K was found to be markedly dependent on pressure; assuming $K \propto p^n$, values of n from 3.9 to 4.3 were obtained, so that the parabolic rate constant was approximately proportional to the fourth power of the pressure.

Since the reaction followed a parabolic relation with time at all pressures, implying that the rates are inversely proportional to film thickness, the controlling process must be diffusion through the oxide film. It is on the latter, therefore, rather than on a surface reaction of the oxide/steam interface, that variations of steam pressure must exert their effect. No certain explanation of the effect can be offered at present, but it seems likely that, under the conditions of the experiments, the composition of the film is significantly changed by variations of steam pressure.

Studies of the equilibrium between steam and bulk aluminium oxides indicate that corundum ($\alpha\text{-Al}_2\text{O}_3$) replaces böhmite ($\gamma\text{-AlO(OH)}$) as the stable phase at about 385°C.⁴ This transition temperature may be rather lower when the oxide forms as a surface film, as is true of the analogous change from bayerite (Al(OH)_3) to böhmite. (For the bulk substances, the transition temperature⁵ is 130°C.; but, on corroding aluminium, böhmite forms the film⁶ above 60°C.). The conversion of AlO(OH) to Al_2O_3 involves the elimination of water, so that at lower pressures the film composition should be nearer $\alpha\text{-Al}_2\text{O}_3$, which might well be more protective than böhmite. If the experimental temperatures were near that of the transition at the pressures studied, a large dependence of composition, and thus of corrosion-rate on pressure, could occur. Preliminary results at 350°C. (and similar steam pressures) suggested not only that rates of corrosion were lower than at 325°C., indicating a more protective film, but also that the dependence on pressure was less, as might be expected further from the transition temperature.

Additional experiments, including a study of the composition of the oxide films, are proceeding and will be reported elsewhere.

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Thermal Decomposition of Hydrogen Peroxide Vapour

KNOWLEDGE of the decomposition of hydrogen peroxide vapour is of considerable importance to the developing understanding of unimolecular reactions and also of the oxidation of many gaseous fuels. McLane¹ and Giguère and Liu² claimed the overall homogeneous decomposition to be first-order. Satterfield and Stein³ claimed that the decomposition occurred by a chain reaction the overall order of which was 1.5. We have carried out an extensive investigation of the decomposition and shown that it is non-chain and second-order (that is, the rate can be expressed as $k[\text{H}_2\text{O}_2][M]$) up to pressures of at least 1 atmosphere of nitrogen). We have further shown that the first step in the decomposition must be the second-order reaction:



Hoare and Walsh⁴ had earlier given reasons why (1) would be expected to be second-order at ordinary pressures. The efficiency of M in bringing about reaction (1) decreases in the order $\text{H}_2\text{O}_2 > \text{H}_2\text{O} > \text{CO}_2 > \text{N}_2 > \text{O}_2 > \text{He}$.

Using our values for the efficiencies of the gases which played the part of M in the work of McLane¹, Giguère and Liu² and Satterfield and Stein³, we have calculated, from the results of these authors, second-order rate constants which, after proper correction for heterogeneous effects, agree excellently one with another and with our own results. The rate constant of (1), when M is H_2O_2 , is found to be $10^{15.4} \exp(-48,000/RT)$ l.mole⁻¹ sec.⁻¹.

A full account of this work will be published elsewhere.

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Deuterium Exchange in Polypeptides

OBSERVATIONS on the rate of deuteration of the NH groups in solutions of proteins in heavy water (see, for example, ref. 1) have shown that in some proteins there is both a fast and a slow exchange, and it has been conjectured that those NH groups which exchange slowly are hydrogen-bonded in α -helix arrangements, whereas the fast reaction is associated with solvated NH groups. This possibility can be more profitably examined in solutions of a simple polypeptide such as poly- γ -benzyl-L-glutamate, where the conditions for α -helical or random, solvated coil forms are now well-known^{2,3}. Doty and Yang³ have shown that in mixtures of dichloroacetic acid and ethylene dichloride, samples of poly- γ -benzyl-L-glutamate of high molecular weight may exist either in α -helix or in random coil forms according to the composition of the solvent.