

absence of any change in the slight influence of a nearby ionizing electron discharge upon the speed of pumping of the carbon monoxide (condensation coefficient), suggests that the gas molecules (neutral or ionized) are not taken up directly by the barium, but are first dissociated into oxygen and carbon. Thus the reaction is one of oxidation in the presence of carbon, and so the qualitative similarity between the behaviour of barium towards oxygen and carbon monoxide is to be expected.

In some details, there are important differences between the reactions in the two cases. In the case of oxygen, it was found⁵ that the first monolayer of oxygen was only taken up if there were nucleation centres in the surface of the barium film. Ordinarily, such centres always exist in the surface of getter films deposited in a fraction of a minute and at pressures greater than 10^{-6} mm. of mercury. Moreover, during the adsorption of the first monolayer of oxygen the speed of pumping increased. In the case of carbon monoxide, the speed of pumping has been found always to decrease during the adsorption of the first monolayer. Furthermore, no nucleation centres are necessary. Once the first monolayer of carbon monoxide has been absorbed, then the film of reaction products grows in a manner which can be explained with the aid of Mott's theory.

A fuller account of this work is being submitted for publication elsewhere.

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State of Iodine in Sea Water

WATER from the upper layers of the ocean contains some 40 $\mu\text{gm./l.}$ of iodine compounds. Sugawara¹ has shown that about half this is iodide, while the remainder is an oxidized form, which he attributes to iodate. We find that various observations are more readily explained on the hypothesis that the oxidized form is principally hypiodous acid.

(1) The ratio of oxidized form/iodide is about unity¹. Calculation from thermodynamic data² shows this to be close to the ratio that would obtain between hypiodous acid and iodide when in equilibrium with atmospheric oxygen, water and hydrogen ions at the pH of sea water. (2) It has been observed that sea water exposed to iodine-free air loses its iodine compounds³; moreover, the iodine content of the atmosphere near the sea⁴ rises to 1–2 $\mu\text{gm./m.}^3$. Data upon the relevant free energies² show that this is about the value to be expected if air is equilibrated with sea water containing its iodine principally as

hypiodous acid and iodide in equal amounts. (The hypiodous acid and iodide take part in an equilibrium to give a trace of iodine which is volatile.) (3) The ratio of total iodine/chloride is higher in warm, partly enclosed sea areas⁵. This is to be expected from the effect of temperature upon the equilibria mentioned in (1) and (2)², which results in a marked increase in the content of volatile iodine molecules when sea water is cooled.

Whereas the hypothesis accounts for these findings, it should be noted that iodate and not hypiodous acid would be the thermodynamically stable form of oxidized iodine in the sea. However, it seems likely that the rate of iodate formation from hypiodous acid, a third-order reaction in near-neutral solution⁶, will be slow at the very low hypiodous acid concentrations in sea water. Together with assimilation by powerfully reducing biological material this factor will tend to prevent iodate accumulating in the sea. On the basis of the hypothesis, and given the necessary thermodynamic data, it should be possible to predict the final oxidation states of marine materials which undergo rapid oxidation-reduction reactions with iodide and hypiodous acid or iodine.

This work and the relevant calculations will be presented in greater detail elsewhere.

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Colorimetric Estimation of Manganese

TETRAMETHYLDIAMINODIPHENYLMETHANE ('tetrabase') has been widely used for the colorimetric estimation of quantities of manganese of the order of 0.01–0.1 $\mu\text{gm.}^{-1}$. As generally applied, the test involves the addition of tetrabase and potassium periodate in excess to a sodium acetate-acetic acid buffer containing manganese in solution. The intensity of the transient blue colour^{1–3}—or more permanent green⁴—so produced is closely related to the concentration of manganese. The nature of the reaction or of its end-products does not appear to have been elucidated, although it is known that manganese hydroxide reacts with tetrabase to produce a blue colour², and it has been suggested that in the presence of periodate, manganese acts as a catalyst in the oxidation of tetrabase³.

In a preliminary study of the reaction it has been found that permanganate and hydrated manganese dioxide are equally effective in the production of the blue colour in the absence of other oxidizing agents. The concentration of manganese necessary to produce unit increase in colour intensity under these conditions is, however, 30–40 times greater than when periodate is present. When manganese and periodate are present in excess, the molar concentration of tetrabase required to produce the same unit increase in intensity is approximately twice that of perman-