to account for the observed rate. Mechanism (c) has been demonstrated to account quantitatively for the observed rate for bicarbonate ion.[12a] The salts which do experience exchange are usually those derived from a weak acid. When exchange is due to reversible anhydride formation, the rate will depend on the rate of the chemical reactions, which are usually rapid, and on the concentrations of the substances which actually take part in the reaction, that is, the amounts of undissociated acid formed by hydrolysis and also the fraction of this in the form of anhydride. The rate depends very critically on these widely variable quantities as can be seen from the calculations given in connection with the chromate ion. In agreement with the expected exchange of salts of weak acids due to greater hydrolysis, sodium metasilicate, borax, sodium carbonate and sodium chromate are known to exchange rather readily. On the other hand, potassium chlorate, potassium perchlorate and potassium sulfate, salts of strong acids, do not undergo exchange under similar conditions. However, in acid solution exchange then occurs due to the shift of equilibrium to form the anhydride. The fact that potassium permanganate and potassium thiosulfate, salts of strong acids, exhibit exchange may be due to relatively large amounts of anhydride present or reactions other than anhydride formation.

Summary

Oxygen exchange between water and Pyrex glass, sodium chromate, potassium hydrogen sulfate, potassium sulfite, sodium metabisulfite, potassium thiosulfate, and potassium permanganate has been studied under conditions of varying temperature and *p*H. The results are discussed in terms of the chemistry of these compounds.

The oxygen exchange between water and sodium chromate is shown to proceed at a rate faster than can be accounted for by the reaction

$$Cr_2O_7^{--} + H_2O = 2HCrO_4^-$$

The rate of oxygen exchange of inorganic oxyanions is related to the acid strength of the corresponding acid. The mechanism of hydrolysis followed by reversible anhydride formation is shown to account for the observed exchange reactions.

RECEIVED AUGUST 3, 1940

Determination of the Surface of Powders

BY FRANK B. KENRICK

Several principles have been employed in the past as a basis for estimating the surface area of irregular solid particles. The following principle is, I believe, new.

It can be shown easily that the average of the areas of the projections of a unit plane area of any shape in all random positions is one-half. The surface of any solid figure in all random positions may be considered as made up of a number of plane surface elements in all random positions, and the sum of the averages of the projection areas of these will therefore be one-half the total area of the figure. In whatever position the figure may be, provided there are no re-entrant angles, exactly half the projection areas of these elements will be masked by the other half, and consequently the average projection area of any such figure in all random positions is one quarter of the total area of the figure. For example, the average projection areas of a sphere of radius 1, a cube of side-length 1, and a plate $1 \times 1 \times 0$ are π, 1.5, and 0.5, respectively. Their actual areas are 4π, 6 and 2.

The average projection areas of a large number of particles in random positions may be determined from planimeter measurements of outlines made on a screen image of a microphotograph of the particles, and this value will approach the average projection areas of particles in all random positions as the number of particles increases. By multiplying this value by four and by the number of particles the true area is given, except for re-entrant angles, and except for any fine-grained roughness which escapes observation in the images. Careful examination of a large number of particles showed that, apart from slight undulations, re-entrant angles were of infrequent occurrence, and examination of a number of large fracture surfaces of glass indicated that the occasional sets of sharp striations formed only a small fraction of the total surface.

Several methods of obtaining random positions of the particles on a slide are described by Mr. Birnie in the next article, "Adsorption of Water Vapor on Silica"; the close agreement of the values obtained by the several methods shows that the methods are satisfactory.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF TORONTO
TORONTO, CANADA

RECEIVED JUNE 13, 1940