

unlike that of normal pseudoglobulin. The predominating constituent, about 95%, gives $s_{20} = 7.4 \times 10^{-13}$ cm./sec./dyne and there is present a trace of component with $s_{20} = 18 \times 10^{-13}$ cm./sec./dyne. The antitoxic preparation used was 35% specifically precipitable by diphtheria toxin.

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OXYGEN EXCHANGE BETWEEN CARBON DIOXIDE, BICARBONATE ION, CARBONATE ION AND WATER

Sir:

The rate of oxygen exchange has been used to study the velocity of the reaction between carbon dioxide and water when the pH is less than 8. In this range the predominating reaction of carbon dioxide is with the solvent molecules rather than the hydroxide ions.¹ Assuming that the reaction proceeds through the formation of H_2CO_3 , and the reversal of this reaction, the equation for the reaction velocity becomes

$$-\frac{d\alpha}{dt} = \frac{k(H_2O)(CO_2)(\alpha - \beta)}{4(CO_2)} \quad (1)$$

where α is the mole fraction of O^{18} in carbon dioxide, and β is the mole fraction of O^{18} in water, which because of the large quantity of water remains constant, and k is the specific reaction rate constant for the reaction between carbon dioxide and water. The equation is of the first order as is usual in these cases.² Moreover, when the water is in excess as, of course, is true in this case, the rate will be independent of the concentration of the reactant.

In our experiments carbon dioxide containing heavy oxygen was dissolved rapidly in water and then samples of this solution were withdrawn from time to time into evacuated vessels in order to separate rapidly the dissolved carbon dioxide from the water. This carbon dioxide was analyzed for its O^{18} content with a mass spectrometer. We find that the velocity constant, $k[H_2O]$, of this reaction is equal to 0.0027 at 0° , the time being in seconds, in good agreement with Stadie and O'Brien.³ There is no salt effect as shown by making the solution 0.045 molar in sodium chloride. Moreover, there is no hydrogen ion cataly-

(1) C. Faurholt, *J. Chim. Phys.*, **21**, 400 (1924).

(2) H. A. C. McKay, *Nature*, **142**, 997 (1938), has shown that this is generally true for exchange reactions.

(3) W. C. Stadie and H. O'Brien, *J. Biol. Chem.*, **103**, 521 (1933).

sis since 0.02 molar hydrochloric acid does not change the rate.

The velocity of exchange of O^{18} between bicarbonate ion and water has been investigated. It appears that the exchange takes place only through the formation of carbonic acid and carbon dioxide, for the reaction takes place much more slowly under these conditions. In this case the rate depends upon the ratio of the carbon dioxide to the bicarbonate concentrations. The kinetic equation is given by Equation (1) above if $4(CO_2)$ is replaced by $2[3(HCO_3^-) + 2(CO_2)]$.

Pure sodium carbonate containing 0.513% of O^{18} has been dissolved in ordinary water. At 25° the time of half exchange in the case of 0.02 molar solution of sodium carbonate is approximately twenty-eight hours, while no exchange was observed when the solution was 0.02 molar in sodium carbonate and 0.04 molar in sodium hydroxide.⁴ The error in our analyses is perhaps less than one per cent. of the percentage of O^{18} present. These results indicate that the reaction proceeds through the formation of the bicarbonate ion.

At 30° we find that the exchange between CO_2 and H_2O is substantially complete in about seven minutes as compared to over an hour at 0° . Such a rapid exchange might account for the decreased O^{18} content found in the experiments by Day and Sheel,⁵ on the oxidation process taking place when heavy oxygen is inhaled by rats. The exchange should be very much more rapid in this case because of the high temperature and the possible effect of carbonic anhydrase.

The results of these experiments will be reported in greater detail later.

(4) T. Titani, N. Morita and K. Goto, *Bull. Chem. Soc. Japan*, **13**, 329 (1938). Our greater analytical precision probably accounts for the difference in results reported here.

(5) J. N. E. Day and P. Sheel, *Nature*, **142**, 917 (1938).

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CRYSTALLINE β -METHYLMANNOFURANOSIDE AND MANNOSEDIMETHYLACETAL

Sir:

Application of the furanoside synthesis developed in this Laboratory [Pacsu and Green, *THIS JOURNAL*, **58**, 1823 (1936); Green and Pacsu, *ibid.*, **59**, 1205, 2569 (1937); **60**, 2056, 2288 (1938); Pacsu, *ibid.*, **60**, 2277 (1938)] to *d*-mannosedithylmercaptal resulted in a 60% yield of α -methylmannofuranoside (m. p. 118–119°; $[\alpha]^{20}_D$