In conclusion it may be pointed out that the conception that the length of the straight chain monoamino monocarboxylic acids and peptides is proportional to the square root of the number of atoms in the chain, involved in our interpretation of δ as linear in the polarization, agrees with the results of recent statistical calculations of the configuration of long chain molecules by Eyring[19] and by Werner Kuhn.[20]

Summary

1. Molecules having two positively charged ammonium and two negatively charged carboxyl groups in the isoelectric condition have been studied. In one molecule the two dipoles are of the same length, in another the one dipole is far longer than the other.

2. Diamino-dithio-dicaproic acid is composed of two molecules of ε-aminocaproic acid combined at the α-carbon atoms by sulfur linkage. Both hydrocarbon chains terminate in an ammonium and a carboxyl group. Electrostatic attraction results in twisting of the chains, and consequently in a relatively small effect on the dielectric constants of solutions and on electrostriction of the solvent.

3. Lysylglutamic acid, a peptide of a diamino and a dicarboxylic amino acid may be considered as constituted of a small dipole, glycylglycine, and a longer one between the ε-amino group of lysine and the γ-carboxyl group of glutamic acid. Electrostatic repulsion between the two positively charged ammonium groups on one side of the peptide linkage and between the two negatively charged carboxyl groups on the other results in a rod-shaped molecule, in which the charged groups are widely separated from each other and the influence on the dielectric constant increment of the solution and the electrostriction of the solvent are maximal.

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[19] Eyring, *Phys. Rev.*, **39**, 746 (1932).

[20] Kuhn, *Ber.*, **67**, 1526 (1934).

[CONTRIBUTION FROM THE FRICK CHEMICAL AND PALMER PHYSICAL LABORATORIES OF PRINCETON UNIVERSITY]

Electrolytic Concentration of Oxygen Isotopes

BY P. W. SELWOOD, HUGH S. TAYLOR, J. A. HIPPLE, JR., AND WALKER BLEAKNEY

As soon as it became apparent that deuterium oxide could be isolated by prolonged electrolytic decomposition of ordinary water, efforts were made to determine whether the density change should all be ascribed to deuterium or in part to the heavier oxygen isotopes. Experiments by Lewis and Macdonald,[1] Selwood and Frost,[2] and Bleakney and Gould[3] showed that no appreciable concentration of O^{18} had taken place even in water of the maximum specific gravity 1.1079.[4] Papers by Washburn, Smith and Frandsen,[5] and by Greene and Voskuyl[6] have indicated, however, an appreciably rapid concentration of O^{18}, and in a recent paper by the late Dr. Washburn and E. R. and F. A. Smith[7] the major part of the density change of ordinary water on preliminary electrolysis is ascribed to heavy oxygen concentration rather than to heavy hydrogen.

The purpose of the present work was to clear up these discrepancies and to determine whether electrolysis is a possible method for the separation of oxygen isotopes even if carried to extreme lengths.

The reason[8] why the earlier workers found no heavy oxygen enrichment in heavy water becomes obvious on consideration of the concentration method used in practice. It is customary, from time to time during the process, to carbonate the concentrated alkali solutions with carbon dioxide and to distil off the partially enriched water. This results in equilibration of the oxygen isotopic ratio to, or nearly to, that of the carbon dioxide used. Any heavy oxygen enrichment is, therefore, defeated as often as carbon dioxide is used.

Experimental

In the present work carbonation was eliminated and neutralization of the solutions prior to dis-

[1] Lewis and Macdonald, *J. Chem. Phys.*, **1**, 341 (1933).

[2] Selwood and Frost, THIS JOURNAL, **55**, 4335 (1933).

[3] Bleakney and Gould, *Phys. Rev.*, **45**, 281 (1934).

[4] Taylor and Selwood, THIS JOURNAL, **56**, 998 (1934). Since this figure was originally published, the writers have on numerous occasions checked it with comparatively large samples of heavy water, and now have confidence in adding another digit, d^{25}_{25} for D_2O = 1.10790 ± 0.00005, the oxygen isotope ratio being normal.

[5] Washburn, Smith and Frandsen, *Bur. Standards J. Res.*, **11**, 453 (1933).

[6] Greene and Voskuyl, THIS JOURNAL, **56**, 1649 (1934).

[7] Washburn, Smith and Smith, *Bur. Standards J. Res.*, **13**, 599 (1934).

[8] Taylor, THIS JOURNAL, **56**, 2643 (1934).

tillation was accomplished with ammonium chloride or hydrogen chloride gas. This simply shifted the equilibration process from the oxygen to the hydrogen. Electrolysis was carried out with nickel anodes as repeatedly described elsewhere. The starting solution was 117 liters of commercial electrolyte about 0.5 N in sodium hydroxide. This was decomposed until only 1 cc. remained. At the start, and from time to time thereafter, samples of the electrolytic oxygen were analyzed in the mass spectrograph.

Results

The results obtained are shown in Fig. 1. This gives the ratio of masses 32 to 34, that is, $O_2^{16}/O^{16}O^{18}$, in the anode gas, plotted against the logarithm of the ratio of initial volume to residual volume of solution. The experimental ratios are all *uncorrected for residual background* but are comparable among themselves. The vertical line through each point is a measure of the maximum probable error as estimated from the spectrographic data.

It will be seen that the heavy oxygen concentration increased steadily but extremely slowly throughout the work. In reducing the volume over one hundred thousand fold, there resulted a concentration of O^{18} of from 0.202% to only 0.222%. In order, therefore, to obtain 1 cc. of 99.5% H_2O^{18} it would be necessary to start with at least 10^{500} cc. of ordinary water, a volume far greater than that of all the water on the surface of the earth. This does not mean that the electrolytic process is useless. As in the case of deuterium, it is probable that a major interest in heavy oxygen will lie in its exchange reactions. Provided the method of analysis is sufficiently sensitive, as the Bleakney mass spectrograph proves to be, even a 10% increase in O^{18} concentration may suffice for many investigations. A deuterium plant such as that at Princeton should be capable, with slight modification, of producing several cc. of such water per week.

Discussion

Of considerable interest is the evaluation of the constant α for O^{16} and O^{18}, that is, the ratio of specific discharge rates. For the present work it is sufficient to define α as the ratio of O^{18}/O^{16} in the solution to that in the anode gas. From our data, α was obtained as follows: the atom per cent. of O^{18} in the anode gas was plotted against the volume of water electrolyzed. Graphical integration gave the total amount of O^{18} in the original 117 liters. (O^{18} in the remaining 1 cc. is of course negligible compared with that in the 117 liters.) We thus obtained the percentage of O^{18} in the starting water, which was found to be 0.204%. The concentration of the first anode gas evolved was 0.202%. Hence $\alpha = 1.0088$ or in round numbers, 1.01.

Greene and Voskuyl found that water formed from electrolytic oxygen and tank hydrogen was 7.7 p. p. m. lighter than normal tap water, while water from air burned in the same hydrogen was 1.1 p. p. m. heavier than normal. It is difficult to see how tank hydrogen could be *heavier* than normal. The 1.1 p. p. m. may possibly be explained by slight fractionation of atmospheric oxygen in the burning–condensation process. In any event their α lies between 1.03 and 1.04.

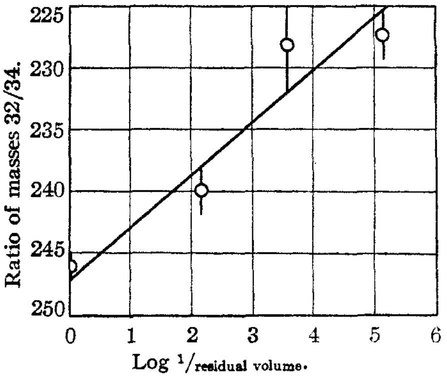

Fig. 1.—Concentration of the molecular species O^{18}–O^{16} on prolonged electrolytic decomposition of water.

A much greater discrepancy is reported by Washburn, E. R. Smith and F. A. Smith. At the start of their electrolysis the following data were obtained: the cell oxygen plus tank hydrogen gave water 13.2 p. p. m. lighter than normal; the cell hydrogen plus tank oxygen (corrected) gave water 7.8 p. p. m. lighter than normal. Assuming the initial ratio O_0^{18}/O_0^{16} to be 0.200×10^{-2} (the precise value chosen will not affect estimation of α) then O_1^{18}/O_1^{16} (in the evolved gas) will be $(2.000 \times 10^{-3})\ (1 - 13.2/222) = 1.881 \times 10^{-3}$. Hence $\alpha = 2.000/1.881 = 1.062$.

In their experiment the water in the cell was renewed from time to time with ordinary water. When equilibrium had been reached, the cell water was treated with ammonia until no further change in density was observed. Of the density increase (in the water of the cell) 32 p. p. m. were found to be due to O^{18} and 28 p. p. m. to D. This gives an α for oxygen of 1.14. According to these results, the separation of oxygen isotopes should become more rapid instead of slowing up as electrolysis proceeds as has previously been suggested.[5]

It is interesting to calculate α for the hydrogen isotopes from the same authors' data. At the start of electrolysis $\alpha_H = 1.65$ and at equilibrium $\alpha_H = 2.4$. These values are much smaller than those usually found (4 to 8) and suggest that the ammonia used for equilibration might not have been of normal isotopic constitution.

Until the mechanism of the rate-determining process is known, it will be impossible to calculate specific discharge ratios with any degree of accuracy. We can, however, show that the ratios experimentally obtained are not inconsistent with reasonable assumptions as to the nature of the process. The process involves liberation from an activated complex of an oxygen atom and the separation ratio from H_2O is given by $e^{-2\Delta E/RT}$ where ΔE is the difference in energy of $O^{18}H$ and $O^{16}H$ and the 2 comes from the fact that to liberate an oxygen atom two such bonds must be broken.[9] Lacking definite information we neglect half quanta associated with the activated state. The difference ΔE in half quanta of the bonds $O^{16}-H^1$, $O^{18}-H^1$ is obtained from Eyring and Sherman's paper and the ratio of reduced masses, and amounts to 17 cal. In this way one calculates a separation ratio of 1.06. Owing to neglect of the half quanta of the activated state, and as in the case of deuterium for which a value some three times in excess of the experimental was obtained, this ratio 1.06 represents a maximum possible rather than a probable ratio and it may also be reduced in practice by recombination or other influence. Of course, our ratios should probably be increased slightly by a mass factor. The separation ratio for the bond $D—O^{18}$ is slightly higher, ΔE being 23 cal. Although the concentration of deuterium in the work reported here exceeded 90% toward the end of the electrolysis yet the analytical method was not sensitive enough to detect any increasing separation efficiency. The apparent increase in Washburn, Smith and Smith's ratio is no evidence for this effect as their deuterium concentration remained low throughout.

The uncorrected ratios of masses 32:34 found in this work for oxygen are all approximately 245. Making corrections for the residual background these results are all consistent with an isotope ratio O^{18} : O^{16} of 500 ± 10 which is the result of many recent American determinations of this ratio.[10] We regard this value for the ratio as much more trustworthy than that reported recently by Muckenthaler,[11] of 1058 ± 69.

The recent publication of Urey and Greiff [THIS JOURNAL, **57**, 321 (1935)] shows that for the isotopic exchange reaction $O_2^{16} + 2H_2O^{18} \rightleftarrows 2H_2O^{16} + O_2^{18}$ heavy oxygen should concentrate in the gas phase. In the present work the O^{18} concentrated *in the liquid*. One reason why the electrolytic process is not very efficient now becomes obvious. We have two opposing tendencies, the electrolytic separation, and that due to the isotopic equilibrium. Of these, the former is slightly more effective. This may also explain the discrepancy between oxygen separation ratios reported here and elsewhere. The effective separation obtained will depend in great measure upon the irreversibility of the anode process and hence upon the nature of the electrode surface.

The writers are indebted to Dr. Henry Eyring for helpful discussions on various aspects of this work.

Summary

Electrolysis of 117 liters of water down to 1 cc. yielded only a 10% increase in O^{18} concentration. The ratio of specific rates of discharge of O^{16} and O^{18} is 1.01. The work is discussed in comparison with other reports and in connection with the probable rate determining process.

PRINCETON, N. J. RECEIVED JANUARY 14, 1935

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(9) Eyring and Sherman, *J. Chem. Phys.*, **1**, 345 (1933).

(10) Smyth, *Phys. Rev.*, **45**, 299 (1934); Taylor and Gould, THIS JOURNAL, **56**, 1823 (1934); Manian, Urey and Bleakney, *ibid.*, **56**, 2601 (1934).

(11) Muckenthaler, *Physik. Z.*, **35**, 851 (1934).