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Concentration of the Heavier Isotopes of Oxygen in Commercial Electrolytic Cells

BY W. HEINLEN HALL AND HERRICK L. JOHNSTON

Lewis and Macdonald[1] found no enrichment of the heavier oxygen isotopes in the electrolyte from a commercial cell, while Webb[2] claims to have found an O^{18} and O^{17} enrichment in commercial electrolyte equivalent to half of the total density increase relative to normal water. No figures were given as to the magnitude of this total density increment but if the electrolyte may be taken as typical of that from old commercial cells Webb's statement would correspond to an oxygen isotope enrichment amounting to 25 or 30 p. p. m. on the density of the water.

Recently, to obtain data on the performance of our "heavy water" plant, we made careful analyses of the heavy oxygen enrichment of the commercial electrolyte on which we began electrolysis.

This electrolyte was donated by the Capital City Products Company of Columbus and came from cells of about 40 gallons capacity, equipped with iron electrodes and operated at five hundred amperes per cell. Following over seven years of continuous operation with no servicing except the addition of distilled water or occasional repairs, the cells stood idle for about two years before the time that they were emptied. The samples which we employed for the oxygen analysis were distilled out of the strong potash solution in iron stills and were not subjected to carbon dioxide treatment or other conditions that might normalize the oxygen isotope ratio, prior to our analysis.

We followed two procedures of analysis: (1) long continued scrubbing with commercial carbon dioxide, introduced into the water through a porous sandstone cup,[3] to normalize the oxygen and (2), separation of the oxygen and hydrogen by electrolysis (to a residual volume of about 5%), with subsequent combustion of the oxygen in a large excess of tank hydrogen. In the latter procedure both the electrolytic oxygen and the tank hydrogen were passed separately over heated platinized asbestos followed by a calcium chloride drying tube; they were then mixed and passed through a train consisting of an explosion trap of sand, a platinized asbestos catalyst and a receiver immersed in cracked ice. To ensure removal of all hydrogen present in the initial water the electrolysis was ordinarily repeated with the first combustion water, although experience proved that this procedure was unnecessary when the catalyst was present in the stream of electrolytic oxygen. Blanks were also run with normal water and certain additional special tests were carried out. The densities of the purified samples[4] were measured to within 1 p. p. m. by means of a totally submerged float.

The results are shown in Table I, in which the third column refers to the relative temperatures at which the submerged float comes to equilibrium.

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

[2] Webb, *Ind. Eng. Chem.*, *News Ed.*, **12**, 63 (1934).

[3] Fractional distillation of the water was prevented by means of a reflux condenser which returned the water carried out as vapor by the escaping carbon dioxide.

[4] *Cf.* (a) Snow and Johnston [*Science*, **80**, 210 (1934)] and (b) Johnston [THIS JOURNAL, **57**, 484 (1935)] for details of the purification and density procedures.

TABLE I

DENSITIES RELATIVE TO NORMAL WATER

Sample	Source of water constituting sample	ΔT	Density difference (in p. p. m.)
1	Commercial electrolyte	+0.189°	51.0
2	(1) Treated with CO_2 for 22 hrs.	+.177	
	(1) − (2)	.012	3.4
3	O_2 from (1) + tank H_2 (excess) (2 successive electrolyses)	− .002	
4	O_2 from normal H_2O + tank H_2 (excess)		
	(a) First electrolysis	− .017	
	(b) Second electrolysis	− .018	
	(3) − (4b)	.016	4.6
5	Tank H_2 burned in air	− .003	

The carbon dioxide method of analysis[5] and the electrolytic method are in good agreement and give about 4 p. p. m. as the contribution of heavy oxygen enrichment to the density of the electrolyte. Within the limits of error this value is also in satisfactory accord with the figure 2 p. p. m. for the steady state enrichment of O^{18} alone, calculated from the isotopic separation factor 1.008 found by one of us[4b] for electrolysis between iron electrodes.

The relationship between the densities of samples (4) and (5) is of interest since these samples were produced from the same hydrogen and from normal oxygen[6] but differ in the particular that hydrogen was in large excess in the combustions associated with (4a) and (4b) while oxygen was in excess in (5). The difference is probably to be attributed to the higher rate at which H_2 reacts with oxygen in comparison with HD.[7] This experimental observation is, of course, important in relation to the interpretation of small density changes in products whose formation involves reaction with gaseous hydrogen. We believe that it accounts, in part, for the comparatively large effect observed by Washburn, Smith and Frandsen[8] in the apparent density of oxygen liberated by electrolysis of a sodium sulfate solution between platinum electrodes, since they burned their oxygen in tank hydrogen.

Summary

The O^{18} and O^{17} enrichment of samples of electrolyte from commercial cells which were in continuous operation for over seven years has been determined by two different procedures: (1) normalization of the oxygen isotopes by continued treatment with carbon dioxide; (2) separation of the oxygen from the hydrogen in the sample by electrolysis with subsequent combination of the oxygen with tank hydrogen. Density measurements by means of the totally submerged float were used to compare the isotopic composition of the various samples of water.

The two procedures, in good agreement with each other, yielded 4 p. p. m. in density as a measure of the "heavy oxygen" enrichment of the commercial electrolyte. This agrees satisfactorily with the electrolytic separation factor of 1.008 for O^{18} alone, determined by Johnston and confirms the observations of Lewis and Macdonald to within the apparent accuracy with which they attempted to measure densities.

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(5) Shortly after this paper was submitted for publication, a paper appeared, by Webster, Wahl and Urey [*J. Chem. Physics*, **3**, 129 (1935)], which shows that carbon dioxide in equilibrium with water containing the normal proportions of the oxygen isotopes is enriched in "heavy oxygen." This enrichment amounts to 10.3 p. p. m. in terms of a specific gravity comparison between water whose oxygen is derived from reduction of the carbon dioxide and the water with which the gas was equilibrated.

Since this raises some question regarding the reliability of our carbon dioxide method of oxygen isotope analysis, we have recently carried out a series of careful tests with carbon dioxide from the same tank used to secure the data with sample (2), Table I. In one test carbon dioxide direct from the tank was reduced, over a nickel catalyst, with an excess of pure light hydrogen produced by electrolysis of deuterium-free water. The specific gravity of the water produced in this reduction exceeded that of deuterium-free water with a *normal* oxygen isotope ratio (ref. 4b) by 9.2 p. p. m. (± about 1 p. p. m.). In a second test the carbon dioxide from the tank was thoroughly scrubbed, before reduction, with normal water, and then dried. The density of the water produced in this reduction, likewise with pure light hydrogen, exceeded that of deuterium-free water with a normal oxygen ratio by 11.2 p. p. m. (±1 p. p. m.). Within limits of error the scrubbing with water produced no change in the density and the average of these two values, 10.2 (±1 p. p. m.) agrees exactly (the exact agreement is fortuitous) with the findings of Webster, Wahl and Urey for carbon dioxide in equilibrium with normal water.

These determinations suggest that the carbon dioxide in the tank has already been equilibrated with normal water. An inquiry sent to the Pure Carbonic Co., who had manufactured the gas through combustion of coke, revealed that the gas had been subjected to a thorough washing with fresh water in its course of manufacture. (A description of the manufacture is given by Wikoff, *Chem. Met. Eng.*, **28**, 5 (1923).) This was evidently sufficient to bring the oxygen contained in the carbon dioxide into equilibrium with that of normal water.

This shows that our procedure in normalizing the oxygen content of the sample of electrolyte was correct in this particular instance and that the results with our sample 2 (Table I) may be compared with those obtained by the second method. This result with the tank carbon dioxide is interesting, and probably is typical since liquid carbon dioxide is produced, primarily, to meet the demands of the carbonated beverage industry and must be thoroughly purified. In general, though, this method of normalizing the oxygen in a water sample cannot be relied upon unless the carbon dioxide is first bubbled through a large excess of normal water.

(6) That a separation of the oxygen isotopes during the electrolysis in (4) is not responsible for the considerable loss in density is proven not alone from independent measurements (Ref. 4b) which show that the electrolysis should produce an effect no larger than 0.2 to 0.3 p. p. m. in the present instance but, directly, from the fact that the second electrolysis (yielding sample 4b) did not lower the density appreciably further.

(7) Melville, *J. Chem. Soc.*, 797–805 (1934).

(8) Washburn, Smith and Frandsen, *Bur. Standards J. Research*, **11**, 453 (1933).

It is found that water formed by combustion of oxygen in an excess of hydrogen is 4 to 5 p. p. m. lower in density than that formed with an excess of oxygen. It is suggested that this observation may have some bearing on the interpretation of the results on apparent oxygen separation, reported by Washburn, Smith and Frandsen.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Molecular Rearrangement of Sulfanilides. I

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In a previous paper,[2] the authors proposed a mechanism of reaction to explain the formation of aromatic amino-sulfides from aniline and similar amines by the action of sulfur in the presence of lead oxide. This mechanism is based on two reactions involving, first, the formation of an intermediate sulfanilide type of compound, which then under the conditions of the experiment undergoes rearrangement to an amino-sulfide. The isolation of such an intermediate from the reaction mixture seemed to present considerable experimental difficulty, so it was decided to prepare a series of analogous compounds containing the -S-NH-linkage within the molecule, and study the conditions controlling their molecular rearrangement.

Zincke[3] has described the preparation of certain compounds of the sulfanilide type. The *o*-nitro derivative, *o*-$NO_2C_6H_4$-S-NHC_6H_5, prepared by the action of *o*-nitrophenyl sulfur chloride upon aniline, is a typical representative. We have prepared this sulfanilide and the corresponding *o*- and *p*-sulftoluidides and studied their rearrangement. We found that *o*-nitrophenylsulfanilide I upon heating at a temperature of 150–160° for six hours gave a small yield of *o*-nitrophenyl *p*′-aminophenyl sulfide, II. This compound was identified by conversion to the corresponding *o*-nitrophenyl *p*′-hydroxyphenyl sulfide, which proved to be identical with the phenol derivative prepared by the action of *o*-nitrophenyl sulfur chloride on phenol.[3]

$NO_2C_6H_4SNHC_6H_5$ I

$NO_2C_6H_4SC_6H_4NH_2$ II

$NO_2C_6H_4SNHC_6H_4CH_3$ III

$NO_2C_6H_4SC_6H_3(CH_3)(NH_2)$ IV

Under similar treatment the *o*- and *p*-sulftoluidides underwent a corresponding rearrangement, the *p*-sulftoluidide III rearranging with substitution *ortho* to the amino group IV. Under the above conditions both compounds gave a dark colored mixture which presented considerable difficulty in purifying and the yield of the sulfide produced by rearrangement was low.

It has been shown previously that the benzidine, methylene[4] and sulfonyl[5] types of molecular rearrangements are greatly accelerated when heated in an acid solution. Here the conditions effecting rearrangement are much milder than when the compounds are heated alone, and are brought about with increased yields. Therefore, our sulfanilides were subjected to a similar treatment, but we found, on warming in a dilute hydrochloric acid solution, instead of undergoing a rearrangement, hydrolysis took place forming *o,o*′-dinitrophenyl disulfide and the hydrochloride of the amine. The same results were obtained if the sulfanilides were heated in the presence of the amine hydrochloride and also on long digestion in glacial acetic acid.

By heating the sulfanilides in the presence of an excess of the corresponding amine we found that it was possible greatly to increase the yield of our rearranged product and obtained it in a form which was much easier to purify. When *o*-nitrophenylsulfanilide, for example, was heated at a temperature of 180–190° for six hours with an excess of aniline, the *o*-nitrophenyl *p*′-aminophenyl sulfide was formed in a yield of 70%. Both the *o*- and *p*-sulftoluidides gave equally as good if not better results. In the case of the *o*-nitrophenylsulf-*o*-toluidide we were able to isolate two rearrangement products which reacted correctly for amino sulfides. The lower melting product was formed in yields about ten times as large as the higher melting material. Thus, it appears,

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[1] A. Homer Smith Research Fellow in Organic Chemistry, 1934–1935.

[2] Moore and Johnson, THIS JOURNAL, **57**, 1287 (1935).

[3] Zincke, *Ann.*, **391**, 57 (1912).

[4] (a) Braun and Kruher, *Ber.*, **45**, 2977 (1912); (b) Cohn and Fischer, *ibid.*, **33**, 2586 (1900); (c) Meyer and Rohmer, *ibid.*, **33**, 250 (1900); (d) Eberhardt and Welter, *ibid.*, **27**, 1804 (1894).

[5] Witt and Truttwin, *ibid.*, **47**, 2786 (1914).