Letters to the Editor

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NOTES ON POINTS IN SOME OF THIS WEEK'S LETTERS APPEAR ON P. 879.

CORRESPONDENTS ARE INVITED TO ATTACH SIMILAR SUMMARIES TO THEIR COMMUNICATIONS.

Density of Light Water: Ratio of Deuterium to Hydrogen in Rain-Water

WE have prepared light water by electrolysing natural water and burning the gases evolved. The water so produced was about 100 parts in 10^7 lower in density than the natural water; on re-electrolysing this, its density was further reduced by about 14 parts in 10^7 , and a third stage in the process reduced the density still further by 12 parts in 10^7 . We have experimental evidence that the third stage light water is almost free from deuterium oxide, which is confirmed by a calculation of the separation obtainable under the actual conditions of the experiment. These observations give, then, a difference in density at 27° C. between the third stage water and rain-water (oxidised to remove organic impurity and twice distilled) of 127 in 10^7 , and imply that there is one volume (or molecule) of deuterium oxide to 8500 volumes (molecules) of hydrogen oxide in rain-water. E. H. and C. K. Ingold, H. Whitaker and R. Whytlaw-Gray¹ found 1 in 9000 for this ratio, and Urey², 1 in 5000. We find the ratio cannot readily be determined with precision because of the difficulty of purifying natural water without changing its density.

In the relative density measurements, the temperature was observed at which a small fused silica float (completely immersed in the water) was in equilibrium, neither rising nor falling. Platinum thermometry was used, and the average error of a determination was about 2 in 10^7 , but for the light water the density during a number of distillations remained constant to 1 in 10^7 . In this respect it proved strikingly different from natural water, which diminished in density each time it was distilled. When a sample of tap water was fractionally distilled, the difference in density between the first and last fractions was 200 in 10^7 , showing that deuterium and hydrogen oxides can be separated by distillation and pointing to the interesting conclusion that, if precise relative determinations of the density of water which had been repeatedly distilled had been made at any time since accurate thermometry has been available, they would have disclosed the fact that natural water is not a simple substance.

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April 23.

¹ NATURE, 134, 661; 1934.

² Rev. Mod. Phys., 7, 40, January 1935.

A Sensitive Polarographic Test for the Absence of Rhenium in Manganous Salts

IN 1925, the present author jointly with V. Dolejšek¹ reported on the occurrence of element No. 75 (Mendeleev's dwimanganese) in manganese salts. However, the discoverers of rhenium, I. and W.

Noddack², and others³ expressed doubts as to whether any measurable traces of this new element could occur in manganese specimens. I investigated the polarographic behaviour of potassium perrhenate and found that it is deposited at the dropping mercury cathode at the potential -1.2 v. from the normal calomel zero (Fig. 1. Curve 2). This method is sensitive enough to show the presence of perrhenate when its concentration is 10^{-5} m. in 1 m. MnCl_2 ⁴ or in alkaline solutions, even if they contain tungstates or molybdates in considerable amounts.

FIG. 1. Polarographic curves for 1 m. manganese chloride (Kahlbaum). (1) pure; (2) with 10^{-5} molar potassium perrhenate; (3) repeated after treatment with hydrogen sulphide.

As the polarographic 'step' at -1.2 v. is not conclusive for the presence of rhenium, so long as other elements are present which are electro-deposited at about that potential (for example, cobalt, iron, nickel, zinc), these were removed from the manganese salts by hydrogen sulphide in the presence of sodium acetate and acetic acid. Some perrhenate was purposely added, which in this way could not be precipitated but merely converted into Re_2S_7 or thioperrhenate⁵. Curiously enough, after this treatment an abnormal increase and shift of the perrhenate 'step' ensued (Curve 3), which was especially marked when the acidic reserve of the buffer had been enlarged by increasing the concentration of the acetate and acetic acid. Thus the perrhenate is easily detectable in a 10^{-6} m. solution; as 0.1 c.c. of the solution suffices for polarographic analysis, detection of 2×10^{-8} gm. (0.02γ) is possible. In the absence of perrhenate, no such effect is observable, even when traces of copper, lead, cadmium, zinc, nickel, cobalt, iron, molybdate and tungstate are present. Although it is not yet ascertained that the described abnormal polarographic effect is specific for perrhenate, its lack can be taken as proof of the absence of rhenium in specimens.

Several specimens of commercial manganese salts were thus investigated polarographically as to their