## In the wake of polywater two new Hydrogen oxides identified

Water covers three-quarters of the earth's surface, and constitutes 50 to 90 per cent of the weight of plants and animals. Nevertheless, widespread though it be, water is one of the very few examples of substances containing only the two elements, hydrogen and oxygen. This paradox is even more striking when one considers that hydrogen is present in abundance in the universe and that oxygen, the most abundant element on earth, accounts for about one-half of the earth's crust in addition to one-fifth of the air around it.

Forgetting water and the various forms of ice and snow, what other hyrogen-oxygen combinations are there? First, there is hydrogen peroxide  $(H_2O_2)$ , a liquid at room temperature, solutions of which decompose easily, by catalysis, to give off oxygen. Such solutions are used as disinfectants, bleaching agents and rocket propellants. But there ends the list of examples from everyday experience.

Entering the realm of curiosities, there is "polywater," a strange variant of water, only recently discovered and still unobserved in any amount as large as a raindrop. Instead of freezing it hardens into a glassy substance when it is at a temperature far below the freezing point of ordinary water. Then, there are a few charged oxygenhydrogen combinations including  $H_3O^+$ , and  $OH^-$  produced in relative abundance in strongly acidic or basic solutions. In addition, there are various "free-radicals", unstable exotic bric-à-brac which are very short-lived on earth because they are so reactive.

Of these, the radical HO<sup>•</sup> is of great astrophysical interest due to its presence in interstellar space, and  $HO_2^\circ$ plays a crucial role in the combustion, explosion or detonation of oxyhydrogen mixtures. The rest is esoterica.

Thus, in marked contrast with sulpher which forms polysulfides from  $H_2S_3$  to  $H_2S_8$ , until quite recently only two stable hydrogen-oxygen compounds were known to exist and there was no known example of a molecule containing more than two oxygen atoms joined by just single bonds.

However, Dr. P. A. Giguère and a research team at Laval University, Quebec City, aided by development and operating grants from the National Research Council of Canada, have succeeded in identifying hydrogen trioxide  $(H_2O_3)$  and also, probably,  $H_2O_4$ , hydrogen tetroxide. The identification of the two new polyoxides, higher members of the homologous series  $H_2O$ ,  $H_2O_2$ , is of great interest and caps a long series of experiments on the chemistry of hydrogen peroxide initiated by Dr. Giguère in 1934 when he was still a graduate student at McGill University under the late Dr. Otto Maass, a pioneer in this field.

This painstaking research has at last resolved a long-raging controversy in the chemistry of peroxy compounds. As far back as 1880, the French chemist Berthelot and later the Russian Dmitri Ivanovich Mendeleev (1895), developer of the periodic classification of the elements, had suggested the existence of higher members of the homologous series made up of water  $(H_2O)$ , and hydrogen peroxide  $(H_2O_2)$ .

No definite proof was forthcoming, however, and these hypotheses were pure speculation. In 1930, with the invention of the electric discharge tube, there was a rebirth of interest in this topic. It was shown that gases, including water vapor, could be dissociated by a high-voltage discharge. When the dissociated vapor was immediately trapped in liquid air, hydrogen peroxide was produced, probably together with unsuspected  $H_2O_3$  and  $H_2O_4$ . Ten years passed before it was suggested that H<sub>2</sub>O<sub>4</sub> was present in order to explain that the product gave off oxygen on warming.

Chemists spent the next twenty years unsuccessfully attempting to prove the existence of hydrogen tetroxide. Direct methods such as X-ray diffraction gave negative results. Indirect arguments to explain the liberation of oxygen from the trapped product were countered by pointing out that the spontaneous decomposition of hydrogen peroxide could have been responsible. Arguments raged back and forth until the Laval chemists made their discovery a short time ago. Ironically, Dr. Giguère was originally one of the sceptics convinced of the



Dr. Paul A. Giguère and one of his coworkers, Mrs. K. Herman, with the apparatus they devised for preparing samples of hydrogen polyoxides in a frozen matrix.

Le Dr Paul A. Giguère et sa collaboratrice, Madame K. Herman, devant l'appareil qui a servi à préparer les échantillons de polyoxydes d'hydrogène piégés à basse température.