gen to the extent of 25 cc. was adsorbed and the desorbed gas then analyzed. It proved to be 45.5% hydrogen and 54.5 deuterium. The closeness of the analyses in successive experiments using first deuterium and then hydrogen points to the establishment of an equilibrium on the adsorbent surface best explained as an equilibrium between hydrogen, deuterium water and deuterowater, the water being present as a unit in the gel structure of the chromium oxide.

This conclusion is further confirmed by the observed influence of temperature on the reaction. At 0° the gas from a partially deuterized gel treated with deuterium for 12.5 hours showed only 11% hydrogen. This was not due to exhaustion of hydrogen from the surface, since, in succeeding experiments at 100°, samples of deuterium were converted to gas containing 47 and 51.5% of hydrogen, respectively, after nine and fifteen minutes of contact. The experiments of Gould, Bleakney and Taylor [*J. Chem. Phys.*, **2**, 362 (1934)] would lead one to expect a much more rapid interchange at 0° if the process involved only adsorbed hydrogen gas and deuterium.

Similar experiments with zinc oxide (*ex* oxalate), in the preparation of which no hydrogen gas was used, point also to water as the source of the hydrogen. Our experiments indicate a much more rapid exhaustion of the hydrogen source in this case than with the gel structure. Hydrogen production may be renewed on such exhausted surfaces on addition of water vapor. Platinized asbestos when first treated with deuterium also shows hydrogen formation, slower than on the gel and also exhausted by continued treatment with deuterium.

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RECEIVED JULY 17, 1934

LIQUID-LIQUID EQUILIBRIA INVOLVING HEAVY WATER

Sir:

Since deuterium water is not so good a salt solvent as ordinary water [Taylor, Caley and Eyring, THIS JOURNAL, **55**, 4334 (1933)], we examined the effect of increasing deuterium content on the lower consolute temperature of nicotine and water and on the (upper) consolute temperature of phenol and water. As expected, the former was lowered and the latter raised as the deuterium content of the water increased. The amount of the lowering of the critical solution temperature of nicotine and water was for 3.9% D, 0.28°; and for 10.6% D, 0.72°. For phenol the corresponding increases were as follows: 3.89% D, 0.43°; 4.12%, 0.50°; 5.81%, 0.71°; 10.62%, 1.24°; 47.20%, 5.58°. The temperature increases in the case of phenol are linear in the % D so that an extrapolation to 100% D is possible. The indicated temperature rise is about 11.8°. No attempt was made to determine the extent of the H-D exchange in these experiments, but it is probable that the hydroxyl and amino hydrogen atoms exchanged completely while the rest did not. A single attempt to show a significant change in the isotopic composition of water as a result of consolution with phenol and subsequent unmixing was unsuccessful.

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RECEIVED JULY 16, 1934

OXYGEN ADDITION COMPOUNDS OF ACETYLENES

Sir:

We have recently found that many acetylenes acquire distinct oxidizing properties after coming in contact with air or oxygen. The acetylenes studied have been mainly of the types $RC\equiv CH$, $RC\equiv CR'$ and $RC\equiv CX$, where R and R′ represent alkyl and aryl groups, and X denotes a halogen. Although these acetylenes have been prepared by widely different methods, a large number of them upon exposure to air for several months contain almost the same amount of oxidizing agents. It is improbable, therefore, that the oxidizing properties of the acetylenes are caused by traces of olefins, for equal quantities of olefins would certainly not be formed by the various methods of preparation. It is conceivable that the acetylenes first polymerize, yielding olefinic derivatives which form peroxides. However, mono-alkyl and di-alkyl acetylenes contain very nearly the same amounts of peroxides after exposure to air for equal periods of time. Consequently, it is probable that the acetylenes themselves form peroxides. The similar concentrations of peroxide in many of the acetylenes may be due to a rearrangement of the peroxide into some more stable form when a certain definite concentration is reached. This hypothesis is supported by the ease with which the peroxides are destroyed by mild oxidizing agents.

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RECEIVED JULY 25, 1934

OXYGEN ISOTOPE SEPARATION BY CHEMICAL REACTION

Sir:

A recent report by W. R. Smythe [*Phys. Rev.*, **45**, 299 (1934)] gives the $O^{16}:O^{18}$ ratio in oxygen obtained by the thermal decomposition of lead peroxide as 503 ± 10. He suggested that there might be some selectivity in the decomposition of the peroxide, favoring O^{16} and making his ratio too high. Since J. Krustinsons [*Z. Elektrochem.*, **40**, 247 (1934)] has recently shown that the decomposition of lead peroxide involves a series of solid solutions, there was a distinct possibility that isotope separation might in this case occur. Ordinarily, decomposition processes in solids occur only at interfaces between two phases and this limitation of reaction might well mask any selective reactivity of isotopes. We have, therefore, decomposed 450 g. of lead peroxide in a system which had been heated and evacuated at 235°. On raising the temperature to 270°, a sample of oxygen (I) was collected by means of a Sprengel pump. Four other samples were collected over a period of days and a final sample (VI) when the residual solid was practically all yellow in color, after a total decomposition time of sixteen days, the temperature having been raised slowly to 310°. An analysis of the first and last samples by Dr. W. Bleakney, of the Palmer Physics Laboratory, using the mass spectrograph, gave "uncorrected" ratios $O^{16}:O^{18}$ of (I) 468, 470, 472 and (VI) 470, 478, and 468. There is, therefore, no evidence at all of any fractionation of the isotopes. The data are in best agreement with measurements by Manian (Dissertations, Columbia University, 1934), using Bleakney's apparatus, on samples of oxygen from meteorites and potassium chlorate, and for which Manian finally arrived at a corrected abundance ratio of 514 ± 13, the correction (for scattered background) amounting to from 4 to 8%. Smythe's ratio does not differ from those of Manian nor our own.

We have also examined the oxygen released from 100 g. of "Superoxol," a 30% hydrogen peroxide, when treated, at ordinary temperatures, with colloidal platinum prepared by the Bredig method. The first sample (I) was that initially evolved, the last (II) was that remaining in the reaction vessel after completion of reaction and standing overnight. Comparative measurements by Dr. Bleakney under as closely comparable conditions as possible gave for the abundance ratio (uncorrected for scattered background) in these two samples: (I) 462 ± 8; (II) 426 ± 4. There appears, therefore, to be, in this case, a definite isotopic separation of oxygen, the divergence between the two analyses being far greater than anything hitherto found with oxygen analyses in the Bleakney mass spectrograph. The separation indicated is in the direction that would result from a less rapid release of O^{18} from the peroxide. We are extending these investigations to other modes of decomposition of hydrogen peroxide and to other materials yielding oxygen at low temperatures.

We wish to thank Dr. Bleakney for his assistance with the analyses.

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