## NEOPENTYL DEUTERIDE

*Sir:*

Since an intensive study of neopentane and its derivatives is being made in this Laboratory, the importance of preparing and studying neopentyl deuteride is obvious.

A quantity of neopentylmagnesium chloride [Whitmore and Fleming, THIS JOURNAL, **55**, 4161 (1933)] was prepared and this material was divided into two equal portions. One portion was allowed to react with 2.5 cc. of distilled water to give neopentane. The other portion was allowed to react with 2.5 cc. of heavy water (sp. gr., 1.0735) and 6.9 g. (yield, 78%) of a mixture of neopentane and neopentyl deuteride was obtained. The reactions were carried out in the same apparatus in exactly the same manner, the only difference being the substitution of heavy water for ordinary water in the second case.

A 4.5-cc. sample of the neopentane produced in this manner was used to obtain its Raman spectrum. This material yielded a spectrum which was identical with that obtained earlier [Rank, *J. Chem. Physics*, **1**, 572 (1933)] for pure neopentane. A similar sample of neopentane and neopentyl deuteride yielded a spectrum which clearly showed the presence of the deuteride. The carbon deuterium vibration is shown by the appearance of a line at approximately $\Delta\bar{\nu} = 2150$ cm.$^{-1}$ shift from the exciting line, which is in accord with the predictions of simple theory. The spectrum clearly shows that the introduction of the deuterium atom into the neopentane molecule partially removes the vibrational degeneracy of this molecule.

The following physical constants were then determined on the neopentane and the neopentane–neopentyl deuteride mixture, using the same apparatus and technique for both.

**Melting Point.**—The melting points were determined simultaneously and it was observed that the neopentane melted at −21 to −20° and the neopentane–neopentyl deuteride mixture at −22 to −21°. Since these two samples were prepared in precisely the same way as to reagents, conditions and treatment, it appears that the neopentyl deuteride causes a lowering of the melting point of the mixture of about 1°. The purest neopentane that we have had showed a freezing point of −19.5° [Whitmore and Fleming, THIS JOURNAL, **55**, 3803 (1933)].

**Refractive Index.**—Using a Valentine refractometer of the Abbe type (manufactured by the Industro-Scientific Co., Colmar, Penna.; calibration checked by Bureau of Standards) at −7.4° (room temperature, −7.4°), the refractive index of the neopentane was observed to be 1.35375 ± 0.00005 and that of the neopentyl deuteride–neopentane mixture to be 1.35360 ± 0.00005.

**Boiling Point.**—The difference in the two boiling points at 740 mm. was approximately 0.2°, the deuteride having the lower boiling point.

Preparation of pure neopentyl deuteride is in progress, upon which accurate physical constants will be obtained. Extensive studies will be made on this unique compound.

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## THE ISOTOPIC FRACTIONATION OF WATER BY DISTILLATION

*Sir:*

In work with heavy water, particularly in exchange of experiments, distillations are frequently desirable either to separate water from substances dissolved in it, or to purify the separated water. It is perhaps worth while to call attention to the serious effect on the results which may arise from isotopic fractionation during distillation. This effect will not be found, of course, where the entire quantity of water distilled is collected, nor when a truly representative sample is obtained by discarding exactly equivalent amounts of the first and last runnings. Moreover, the work of Washburn [Washburn, Smith and Frandsen, *Bur. Stand. J. Res.*, **11**, 453–462 (1933)], and Lewis [Lewis and Cornish, THIS JOURNAL, **55**, 2616 (1934)], indicates that the effects to be expected on samples approaching ordinary water in composition will be very small in ordinary apparatus at atmospheric pressure. That such effects are far from negligible in dealing with more highly enriched samples is shown by the following results. (1) A sample of 125 cc. volume containing about 3% of the heavier isotope was very carefully purified and then distilled slowly at atmospheric pressure from an ordinary flask surmounted by a simple Vigreux column about 10 cm. long connected to a quartz condenser. The vertical part of the condenser before the bend was about 20 cm. long. Three fractions of the distillate were collected and their specific gravities determined at 25°, with the following results:

| Fraction of distillate | Sp. gr. | Variation from mean, % |
|---|---|---|
| 0.00 to 0.20 | 1.003365 | −2.6 |
| .61 to .77 | 1.003444· | |
| .77 to .96 | 1.003546 | +2.6 |

The index of refraction of the samples was also determined in a Zeiss interferometer and showed a *decrease* from the lightest to the heaviest sample nearly, but not quite, proportional to the density *increase*. (2) In another experiment with 3% heavy water ten successive samples were collected and measured, and all showed a progressive decrease in index of refraction—the total decrease from the first to the ninth amounting to 5.7% of the mean value. The tenth fraction showed a further decrease of 5.8%. When a Widmer column containing a glass spiral 50 cm. long was used (with a different quartz condenser), a difference of over 15% in the apparent concentration of the heavy isotope (as shown by the refractive index) was shown by the second and next to last fractions distilled.

All of these results were obtained at atmospheric pressure. When the pressure was reduced to 10 mm. of mercury or less, a still more striking fractionation (of 2% water) was produced with the aid of an ordinary distilling flask without fractionating column. The first fifth of the distillate contained 32% less heavy isotope than the starting material, and the last fifth about 25% more.

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## EXCHANGE REACTIONS OF HYDROGEN ATOMS

*Sir:*

Approximately 2% heavy water prepared by electrolysis was allowed to dissolve various substances and later separated from them by distillation at atmospheric pressure. After purification the density of the water was found in all cases to have decreased. A slight density loss, found even when the solute contained no hydrogen, was traced to fractionation on distillation, and failure to recover 100% of the distillate during purification. Allowing for this effect, we find as follows: (1) no interchange of hydrogen during brief contact, (potassium chloride) potassium hypophosphite, potassium acetate, sodium benzoate, hydrogen gas; (2) one-third of the hydrogen in the substance immediately exchanged, ethylene glycol; (3) extent of exchange increasing markedly with time of content, potassium acetate, hydrogen gas. The work with hydrogen gas was carried out with the collaboration of Professor Homer Adkins, who kindly placed at our disposal his high pressure hydrogenation equipment. Ordinary electrolytic hydrogen was used in amounts approximately equimolar to the total water present. The results were as follows.

| Run | 1 | 2 | 3 |
|---|---|---|---|
| $T$, °C. | 230 | 220 | 230 |
| Time of contact, hrs. | 1.0 | 9.5 | 9.5 |
| $pH_2$, atm. | 340 | 370 | 370 |
| Ratio at start | 97 | 85 | 82 |
| $H^1H^2O/H^1H^2$ at end | 5.1 | 2.5 | 1.9 |

The ratios are calculated on the assumption that the hydrogen gas used contained 0.02% deuto-hydrogen. (It was obtained from a plant where the electrolyte contains approximately 0.1%.) In the first two experiments no catalyst was added to the bomb, but its walls were perhaps not entirely free from nickel from previous hydrogenations. In the third run a considerable amount of a nickel catalyst prepared according to Raney [Adkins, THIS JOURNAL, **54**, 4116 (1932)] was used. These results agree with Bonhoeffer's [Bonhoeffer *et al.*, *Z. physik. Chem.*, **23B**, 171 (1933); *Naturw.*, **22**, 45 (1934)] on sucrose and sodium acetate, except that we find the hydrogens of the acetate group not wholly inert even when nothing is added to promote enolization. (In one run, after sixty-six hours of contact, 34% of the hydrogen in the salt had apparently exchanged.)

Our results with hydrogen do not yet indicate the position of equilibrium. The work is being continued.

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