

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 contact, 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 <sub>2</sub> , atm.   | 340 | 370 | 370 |
| Ratio at start   | 97  | 85  | 82  |
| H <sup>1</sup> H <sup>2</sup> O/H <sup>1</sup> H <sup>2</sup> at end | 5.1 | 2.5 | 1.9 |

The ratios are calculated on the assumption that the hydrogen gas used contained 0.02% deuterium. (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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