

## The Fractionation of the Oxygen Isotopes in an Exchange Reaction

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Citation: [The Journal of Chemical Physics](#) **3**, 129 (1935); doi: 10.1063/1.1749608

View online: <http://dx.doi.org/10.1063/1.1749608>

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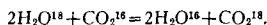
## LETTERS TO THE EDITOR

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### The Fractionation of the Oxygen Isotopes in an Exchange Reaction

Recently Urey and Greiff<sup>1</sup> have presented theoretical calculations on the equilibrium constants of exchange reactions involving the isotopes of the lighter elements and among others the exchange reaction,



At 0°C the equilibrium constant for this reaction is found to be 1.097, which gives for the fractionation factor for this reaction 1.047, the O<sup>18</sup> being concentrated in the carbon dioxide. This reaction is well suited to the separation of the oxygen isotopes by using counter-current scrubbing apparatus similar to fractionation columns in construction.

In this note we wish to report the experimental confirmation of the fractionation factor calculated from theory. The method consisted in passing carbon dioxide gas from a tank through three spiral wash bottles in series containing water from which the deuterium had been largely removed. The gas was then mixed with deuterium-free hydrogen gas prepared electrolytically and the mixture passed over a supported nickel catalyst to convert the carbon dioxide to methane and water. The specific gravity of the water in the wash bottles and the water produced catalytically from the carbon dioxide were compared. The deuterium-free water used in these experiments was prepared by electrolyzing a large volume of ordinary water, collecting the first 10 percent electrolyzed, then re-electrolyzing this and catching the first 10 percent re-electrolyzed. The fractionation factor of these cells runs between 9 and 10 and hence most of the deuterium should have been removed. The specific gravity of the water at 25° was 0.999979, determined with a pycnometer.\* The specific gravities of the water from the wash bottles and from the carbon dioxide were compared by a pressure float method described by Gilfillan.<sup>2</sup> The determination of the specific gravity of the water from the wash bottles by this method agreed with the pycnometer value given above. Three determinations of the specific gravity of the water from the carbon dioxide gave a mean value for the specific gravity of 0.9999892, giving a difference in the two specific gravities of 10.2 parts per million with an error of not over 1 part per million. The calculated difference in density is 10.3 parts per million using 1.047 as the fractionation factor. The difference between these two values is within the experimental

limit of error and also the probable error in the calculations as estimated by Urey and Greiff.

We are at present constructing a counter-current scrubbing apparatus with the object of separating the oxygen isotopes by the method outlined by these authors.

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Columbia University,  
January 16, 1935.

<sup>1</sup> Urey and Greiff, J. Am. Chem. Soc. **57**, in press (January, 1935).

<sup>2</sup> Gilfillan, J. Am. Chem. Soc. **56**, 406 (1934).

\* This water was kindly prepared for us by Dr. W. G. Brown and A. F. Daggett, who will describe their plant in a forthcoming publication.

### A Correction and Addition to the Discussion of the Ground State of H<sub>2</sub>

Our recent paper<sup>1</sup> on the ground state of H<sub>2</sub> contains a minute error, detected on the eve of publication, about which we wish to make a more complete statement. When correctly computed the energies corresponding to the wave functions defined in that paper come out lower than the values there given by 0.003 e.v. for the 11-term function and by 0.001 e.v. for the 13-term function at the equilibrium distance. Furthermore, the functions are not accurately normalized; they should be reduced by approximately 0.05 percent, or the corresponding correction applied to the result of any calculation based on their published form. The 5-term function and the corresponding energy value were not affected by the error. In principle, it would be possible to improve the functions (aside from the question of normalization) by revising the ratios of the coefficients, but we have not undertaken this, as it is clear that the resulting improvement would be quite negligible.

The largest binding energy computed was -4.698 e.v. Correcting this by 0.006±0.003 e.v. for the effect of nuclear motion,<sup>2</sup> and making an allowance of -0.03±0.01 e.v.<sup>3</sup> for the improvement available from the addition of other terms, we get -4.722±0.013 e.v. as the binding

energy of  $H_2$  at the potential minimum. Correcting for the zero point vibration we then obtain for the dissociation energy of  $H_2D_{H_2} = 4.454 \pm 0.013$  e.v., as the probable result of a complete theoretical treatment of the problem.

We should like to mention also an unsuccessful attempt to improve our method by the introduction of the Wang function as a term in the series. For larger separations of the nuclei this would certainly be helpful, but for those under consideration this was not the case. The computations became somewhat more complicated through loss of uniformity in character, and no results were obtained on introduction of this function which could not be duplicated

by the addition in its place of one or two terms of the standard form.

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ALBERT SPRAGUE COOLIDGE

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Mallinckrodt Chemical Laboratory,  
Harvard University,  
January 14, 1935.

<sup>1</sup> H. M. James and A. S. Coolidge, J. Chem. Phys. 1, 825 (1933).

<sup>2</sup> A first order correction for this effect entered our work through the comparison of the fixed nucleus problem for both molecule and atoms.

<sup>3</sup> This differs from our previous estimate, which was  $-0.03 \pm 0.02$  e.v. An example of the method used in estimating convergence is contained in a paper on the  $1s2p\ ^3\Sigma_u$  state, now in preparation.