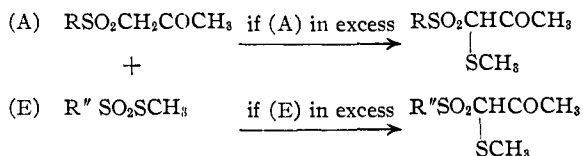


It is evident that this reaction possesses the additional advantage of applicability to the preparation of unsymmetrical<sup>5</sup> methylene disulfones, and in developing it to that end a most interesting type of radical exchange has been discovered<sup>6</sup>



Results already obtained indicate that the exchange is  $\text{R}''\text{SO}_2$  for  $\text{RSO}_2$  (rather than  $\text{R}''$  for  $\text{R}$ ). Further, where  $\text{R}$  and  $\text{R}''$  are both aryl (or both alkyl), the exchange of radicals is a mass action effect, but while alkyl sulfonylacetones are readily converted to aryl derivatives, the reverse has not been observed.

Obviously, if  $\text{R} = \text{R}''$ , the exchange phenomenon is not observed, and as methylene di-*n*-butyl disulfone now figures in the literature with two widely discrepant melting points,<sup>7</sup> I would suggest that the sulfonyl acetone route might be used to give an independent confirmation of one or the other value.

(5) Posner, *Ber.*, **36**, 200 (1903).

(6) *J. Chem. Soc.*, 1819 (1932); 306 (1933).

(7) Stutz and Shriner, *Ref. 1*, m. p. 96°; Whitner and Reid, *THIS JOURNAL*, **43**, 638 (1921), m. p. 182°.

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DAVID T. GIBSON

RECEIVED MAY 2, 1933      PUBLISHED JUNE 6, 1933

### THE FRACTIONATION OF ISOTOPES BY ELECTROLYSIS

Sir:

In view of recent communications regarding the isotopic fractionation of the elements of water by electrolysis [Washburn and Urey, *Proc. Nat. Acad. Sci.*, **18**, 496 (1932); Lewis, *THIS JOURNAL*, **55**, 1297 (1933); Washburn, Smith and Frandsen, *J. Chem. Phys.*, **1**, 288 (1933)] it is of interest to record that in 1923 Dr. Malcolm M. Haring, working under my direction at Columbia University, achieved a slight fractionation of mercury by the same method. Electrolysis of an acid solution of mercurous nitrate, using a low voltage and low current density, gave mercury with a density only 0.999981 that of ordinary mercury. This value was the average of fourteen different electrolyses. Parallel experiments in which a high voltage and high current density were employed gave mercury with density unchanged.

The reduction in density, it will be seen, was only 19 parts per million, which represented three times the average deviation of the individual results. The greatest difficulty encountered in the whole investigation was

the exact setting of the mercury level in the pycnometers and, although the error involved thereby was minimized by repeating each setting five times and averaging the results of the five weighings, the probable error involved still amounted to 7.5 parts per million. This fact, together with the disappointingly small change (0.004 unit) in the average atomic weight of the electrolyzed mercury, discouraged us from proceeding further at the time. The results of the work were recorded by Dr. Haring in a Columbia University dissertation printed in 1924, but have not hitherto been given further publicity.

I have always been convinced, however, of the reality of the indicated fractionation and, in the expectation that more conclusive results would be obtained with a lighter element than mercury, Mr. James McLaren of Syracuse University began a systematic study of the electrolytic method of isotopic fractionation under the direction of myself and Dr. E. B. Ludlam at the University of Edinburgh in 1930. A considerable amount of work had been done on lithium, but no final results attained, when the discovery of the isotopic character of hydrogen turned our attention early in 1932 to that element, which obviously offered still greater chances of success. Spectrographic evidence suggesting that the proportion of the heavier hydrogen isotope in the first fraction of the electrolysis of water was less than in ordinary hydrogen was obtained, but while confirmatory experiments were in progress the more striking changes revealed in the last fractions, alluded to in the first paragraph of this letter, have been announced, and anything that we may now have to report regarding the other end of the process can only be of the nature of an anti-climax.

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#### THE PARA-HYDROGEN CONVERSION AT PARAMAGNETIC SURFACES

*Sir:*

In extending the investigations of Taylor and Sherman [THIS JOURNAL, 53, 1614 (1931); *Trans. Faraday Soc.*, 28, 247 (1932)] on the function of van der Waals and activated adsorption of hydrogen on the para-hydrogen conversion, we have found that, modifying the earlier results, there is a whole series of surfaces on which, at liquid air temperatures, the van der Waals adsorption of hydrogen is accompanied by extremely rapid conversions of ortho to para hydrogen. Chromium oxide gel was the first of these which we discovered with the assistance of Mr. J. Howard, who has been investigating the adsorption of hydrogen on this substance. More recently we have added to the list a crude cerium oxide, probably containing