

COMMUNICATIONS TO THE EDITOR
DISCONTINUITIES IN ADSORPTION ISOTHERMALS

Sir:

We shall await with much interest the further details of the results on discontinuities in adsorption isothermals forecasted in the communication recently made by Messrs. Benton and White [THIS JOURNAL, 53, 2807 (1931)]. In particular, the hypothesis offered in explanation of the discontinuous phenomena attracts our attention, as it is similar in certain respects to one which we were considering seriously about two years ago. The following is an extract from a report of a lecture given by one of us in the University of Oxford in December, 1929.

"The speaker finally briefly discussed possible explanations for the discontinuous structure of these isothermals which his experiments seemed to make probable. As a working hypothesis only (for there are difficulties and objections to be overcome and far more experimental work is needed) he inclined to the following. Adsorption on charcoal starts out from 'active centres,' from which 'islands' of sorbate spread out, in the sense of Polanyi and Goldmann. An 'island' is actually composed of a series of concentric rings. The completion of a ring and the commencement of a new one is marked by a 'break.' The spatial position of the rings with respect to the active centres is not invariable—they are closer in at high temperatures and with low-boiling sorbates than at low temperatures or with high-boiling sorbates. So Polanyi's 'constant potential surfaces' (or lines) have no connection with the breaks."

These suggestions represented an attempt at an explanation of what appeared to us at the time to be the most striking features of our results, *viz.*, the apparent facts that, whatever the exact nature of the charcoal, whether using the vapor of carbon tetrachloride, of carbon disulfide or of water, and whether working at 25° or at 100° (*a*) the lowest of the observed breaks occurred at, or very near, a pressure of 0.1 mm., and (*b*) there was a very considerable degree of concordance between the pressures at which subsequent breaks were observed. On the other hand, we had been unable to discover any regularities in the increment of sorbate taken up between successive breaks.

Subsequent work with charcoal and various vapors has shown that the pressure regularities referred to are not as well marked as then appeared. On the other hand, unpublished work with silica gel has shown great regularities in the *q* increments between successive breaks, their exact nature varying with the nature of the adsorbed vapor, while the pressure values at which breaks occur are very reproducible, although their relations to one another have not yet been completely analyzed. And it may be added that a former colleague of ours has obtained, and hopes soon to

publish, very strong evidence that adsorption isothermals given by charcoal-aqueous solution systems may also show discontinuous structure.

The more homogeneous nature of the surfaces of finely divided metals and of silica gel as compared with charcoal, together with the complications due to the gradual elimination of gas from the surface of the latter during adsorption, is presumably responsible for the more regular and uniform results obtained with the former adsorbents.

KING'S COLLEGE
LONDON, ENGLAND
RECEIVED SEPTEMBER 28, 1931
PUBLISHED DECEMBER 10, 1931

A. J. ALLMAND
L. J. BURRAGE

A NOVEL MODIFICATION OF METHYL-*D*-XYLOSIDE¹

Sir:

During a recent preparation of the methylglycosides of *D*-xylose, a novel modification was isolated. Having condensed thirty-five grams of the sugar with methyl alcohol by refluxing for two hours under the usual conditions [Hudson, THIS JOURNAL, 47, 265-268 (1925)], and having removed a 6-g. crop of the β -methyl-*D*-xyloside, we concentrated the filtrate to a thick sirup which was then dissolved in four volumes of amyl alcohol. Overnight 20 g. of crystals of a new substance separated. After one recrystallization from methyl ethyl ketone, its $[\alpha]_D^{21}$ value was $+104.4^\circ$ in water (concn. 2%) and this rotation was not changed by two subsequent recrystallizations. The m. p. is $89-91^\circ$. The crystals are exceptionally clear and well-formed prisms with pyramid faces at one end, quite different from the crystals of the well-known β -methyl-*D*-xyloside ($[\alpha]_D^{20} - 65.5^\circ$) or α -methyl-*D*-xyloside ($[\alpha]_D^{20} + 154.5^\circ$).

The properties so far described might well lead one to the conclusion that this substance is probably a new chemical isomer of the known methylxylosides, but this view proved erroneous on further test. Acetylation of the substance with acetic anhydride and pyridine in the cold gave a product which was resolved into the tetra-acetates of the known α - and β -methylxylosides, the former predominating. Moreover, a determination of the rate of hydrolysis of the new substance by 0.05 *N* hydrochloric acid (approximately 1 g. in 25 cc.) gave $k = 0.00121 \pm 2 \times 10^{-5}$ at 99° (min. and dec. logs). Redeterminations of the rates for the ordinary alpha and beta forms under identical conditions gave $k = 0.00151 \pm 2 \times 10^{-5}$ and $k = 0.00286 \pm 4 \times 10^{-5}$, respectively. Since the two latter substances have opposite signs of rotation and the rotation of xylose lies between these values, a mixture of them would have a rate of hydrolysis apparently smaller, when determined polarimetrically, than that of either component. An actual mixture of the ordinary alpha and beta forms in the ratio of seven to two, gives a specific rotation of $+105.4^\circ$ and shows an

¹ Publication approved by the Surgeon-General, U. S. Public Health Service.