

their final tables, in the two papers referred to, below 0.0125 *m* (0.00625 *m* in the case of sodium bromide) should be designated as extrapolated and not as interpolated values. Although the values which they record for the final concentrations are very likely correct, it is, nevertheless, desirable to point out that they do not constitute measured values, but involve the acceptance of the validity of the Debye-Hückel theory. This theory is without doubt the best to employ at the present time, yet there have been examples in which specific individual characteristics have been obscured by its use at concentrations which, at the time, were thought to be sufficiently dilute for application.

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THE OXYGEN VALENCE ANGLE AND THE STRUCTURE OF GLUCOSE AND RELATED COMPOUNDS

Sir:

During the last ten years an extensive series of investigations has been carried out on the synthesis and structure of various oxygen-bridged ring compounds from the point of view of elucidating the structure and properties of glucose and polysaccharides. During the progress of this work, it has become more and more evident that the assignment of the same tetrahedral angle to both the oxygen and carbon atoms is incorrect and that many of the anomalies found in the study of carbohydrate chemistry are due to the lack of recognition of this factor.

In the case of furanose and pyranose ring forms of the sugars this point has also been stressed by Haworth, Cox and other workers.

During the last three years a careful study has been made on the electric moments of ethylene oxide, propylene oxide, trimethylene oxide, tetrahydrofuran (tetramethylene oxide) and tetrahydropyran (pentamethylene oxide), and the oxygen valence angles calculated in each case. These have been determined as follows.

OXYGEN VALENCE ANGLES IN CYCLIC ETHERS		
Compound	Moment ($\times 10^{18}$)	Oxygen valence angle
Ethylene oxide	1.88	77°
Propylene oxide	1.88	65 ^{ca}
		77°
Trimethylene oxide	2.01	102°
Tetrahydrofuran	1.71 ^a	105°
		ca. 100 ^{ca}
Tetrahydropyran	1.87	88°

^a Smyth and Walls, THIS JOURNAL, 54, 3230 (1932).

The "normal" oxygen valence angle has been determined from these measurements as $90 \pm 5^\circ$. This value is the first experimental confirmation, by electric moment measurements, of the same angle suggested by the quantum mechanical considerations of Pauling. From these results it can be definitely shown that the pyranose ring of carbohydrates and related polysaccharides represents a "strainless" puckered ring system in which the carbon valence linkages are tetrahedral while the oxygen valence angle is approximately 90° . The pyranose ring has therefore a di-planar structure with all the carbon atoms in one plane and the oxygen atom in a different plane from the carbon atoms. On the other hand, the furanose ring structure of similar compounds represents a strained flat ring in which both the carbon and oxygen valence angles are distorted. The relative instability of furanose as compared with pyranose rings thus finds a satisfactory explanation. A full account of this work will be published in the near future.

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NICKEL BY THE RANEY PROCESS AS A CATALYST OF HYDROGENATION

Sir:

There is now available (Murray Raney, Chattanooga, Tennessee, U. S. Patent 1,628,190, May 19, 1927) a pure nickel catalyst which under some circumstances is preferable to the "nickel on kieselguhr" type of catalyst [Covert, Connor and Adkins, *THIS JOURNAL*, **54**, 1651 (1932)]. The Raney catalyst is prepared by alloying equal parts of nickel and aluminum and then dissolving out the latter with aqueous sodium hydroxide. Both the alloy and the metallic nickel suspended in water are commercially available. The latter is satisfactory for many hydrogenations but a more active catalyst may be prepared from the alloy by the following procedure. Three hundred grams of the finely ground nickel-aluminum alloy was added slowly (two or three hours) to a solution of 300 g. of sodium hydroxide (80%) in 1200 ml. of distilled water, contained in a 4-liter beaker surrounded by ice. The mixture was then heated on a hot-plate for four hours with occasional stirring at $115-120^\circ$. A further 400 ml. of a 19% solution of sodium hydroxide was added and the mixture kept at $115-120^\circ$ for about three hours or until bubbles of hydrogen were no longer evolved, after which it was diluted to a volume of three liters. The clear solution of sodium aluminate was decanted, and the nickel washed by decantation six times, and then alternately by suspension and by washing on a Buchner filter with distilled water until the filtrate was neutral to litmus. The nickel was then washed three times with 95% ethanol and kept under