This Week's Citation Classic

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Glasoe, PK& Long F A. Use of glass electrodes to measure acidities in deuterium oxide.
J. Phys. Chem. **64**:188-9, 1960.
[Cornell University, Ithaca, NY]

The deuterium analog of pH can be measured in deuterium oxide solutions with a glass electrode which has been standard-ized to read pH in an aqueous solution. The pD is calculated from the relation: pD = pH reading + 0.41. This relation gives correct pD values with ordinary commercial elec-trodes of a variety of types and holds over the pD range for which the glass electrode functions normally in water solutions. [The *SCI®* indicates that this paper has been cited over 540 times since 1961.]

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"Shortly after pure deuterium oxide ('heavy water') became available, measurements of the dissociation of deuteroacids in deuterium oxide were made using deuterium gas electrodes. It was found that the deuteroacid had a higher pK than its hydrogen counterpart and that there was a slight dependence of pK_D- pK_H on the value of pK_H. Long and Dahlgren measured pK_D for maleic acid and found an abnormal-ly high value of the pK difference for the first ionization of this acid and an abnor-mally low difference for the second ioniza-tion.[1] It was suggested that these unusual differences in pK_D - pK_H were due to the in-tramolecular hydrogen bond in the monoa-nion of maleic acid. These measurements were made with a quinhydrone-silver, silver chloride cell.

"Somewhat surprisingly, given its great simplicity, application of the glass electrode to measurements in deuterium oxide had not been reported and we decided to in-vestigate. Since good data were available for pK_D for deuteroacetic acid, we chose acetate buffers in deuterium oxide as a standard for the measurements. A commer-cial glass electrode and a calomel reference electrode, both containing water solutions, were connected to a pH meter and the meter was standardized to read pH in a water buffer. When this electrode combination was applied to acetate-deuteroacetic acid buffers in deuterium oxide, the relation pD = pH meter reading + 0.41 led to the correct pK_D for acetic acid. Further studies revealed that this simple relation applied to solutions in deuterium oxide over the entire useful range of glass electrodes and held for a wide variety of types of glass electrodes.

"It is general experience that glass elec-trodes which have been out of water for some time require a soaking period before they will give stable readings. It was therefore surprising to find that a glass elec-trode which had been equilibrated in a water buffer came to equilibrium im-mediately when placed in a deuterium oxide buffer. Apparently, the necessary new surface-solution equilibrium is established very rapidly. Since it is well known that glass electrodes vary in their asymmetry poten-tials and must be calibrated individually to measure pH, another surprising result was that the same relation for pD applied to other glass electrodes, including those designed for use in the high pH region.

"Some years later, Gary, Bates, and Robinson, working at the Bureau of Stand-ards, established a pD scale using a deuterium gas electrode and confirmed our results with measurements with a glass elec-trode in the pD buffer which they had established as their standard.[2] The simplici-ty and general applicability of glass elec-trode measurements for pD has been par-ticularly valuable in examination of kinetic isotope effects as an aid to determining reaction mechanisms. The procedure has apparently been especially useful for studies in biological systems.

"The success of this research was particularly gratifying to one of us (PKG) because it served as the starting point of an undergraduate research program which brought to his college a series of research grants and may rich experiences with under-graduate students over a period of 15 years. This follow-on research activity has been an important ingredient in our education of chemists, and furthermore, it has been a lot of fun."

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1. **Long F A & Dahlgren G .** Relative hydrogen bonding of deuterium. I. Ionization constants of maleic and fumaric acids and of their nonethyl esters in H_2O and D_2O. *J. Am. Chem Soc.* **82**:1303-8. 1960.
2. **Gary R, Bates R B** & **Robinson R A.** Second dissociation" constant of deuteriophosphoric acid in deuterium oxide from 5-50°. Standardization of a pD scale. *J. Phys Chem.* **68**:38 06-9. 1964.