Acid Base Theories: Svante Arrhenius

I. Introduction Svante Arrhenius was one of the towering giants of chemistry in the years surrounding the turn of the century. His most important contribution to chemistry was also his first - the idea of electrolytic dissociation. This idea, first published in 1883 and in refined form in 1887, was the mainstay of his doctoral dissertation. It was the source of much hurt in his life. The basic idea is that certain substances remain ionized in solution all the time. Today, everyone accepts this without question, but it was the subject of much dissention and disagreement in 1884, when a twenty-five year old Arrhenius presented and defended his dissertation. He was bitterly disappointed when the dissertation was awarded a fourth class (non since laude approbatur - approved not without praise) and his defense a third class (cum laude approbatur - approved with praise). Essentially, he got a grade of D for the dissertation and a C for his defense. He could not obtain a job within his native Sweden, but he did get a travel grant and worked outside the country for several years. He did return in 1891, but even in 1895, his elevation to Professor of Physics was bitterly opposed as was his overdue election to the Swedish Academy of Sciences in 1901. However, he received the 1903 Nobel Prize in Chemistry for his electrolytic dissociation theory and that effectively ended public criticism. Considering the rejections and the criticisms over the years, Arrhenius must have been very, very happy to win the Nobel. The ChemTeam would have been and it would bet that you would also have been, dear reader!The Acid Base Theory Arrhenius published two articles on acids and bases, one in 1894 and the other in 1899. However, the ChemTeam thinks the actual first statement of the theory is in his 1887 publication concerning the electrolytic dissociation theory. The ChemTeam is working on finding out. In any case here it is: Acid - any substance which delivers hydrogen ion (H+) to the solution.

Base - any substance which delivers hydroxide ion (OHÂ¯) to the solution. Here is a generic acid dissociating, according to Arrhenius: HA ---> H + + AÂ¯ This would be a generic base: XOH ---> X+ + OHÂ¯ When acids and bases react according to this theory, they neutralize each other, forming water and a salt: HA + XOH ---> H2O + XA Keeping in mind that the acid, the base and the salt all ionize, we can write this: H+ + AÂ¯ + X+ + OHÂ¯ ---> H2O + X+ + AÂ¯ Finally, we can drop all spectator ions, to get this: H+ + OHÂ¯ ---> H2O These ideas covered all of the known acids at the time (the usual suspects like hydrochloric acid, acetic acid, and so on) and most of the bases (sodium hydroxide, potassium hydroxide, calcium hydroxide and so on). HOWEVER, and it is a big however, the theory did not explain why ammonia (NH3) was a base. There are other problems with the theory also. III. Problems with Arrhenius' Theory 1) The solvent has no role to play in Arrhenius' theory. An acid is expected to be an acid in any solvent. This was found to not be the case. For example, HCl is an acid in water, behaving in the manner Arrhenius expected. However, if HCl is dissolved in benzene, there is no dissociation, the HCl remaining as undissociated molecules. The nature of the solvent plays a critical role in acid-base properties of substances. 2) All salts in Arrhenius' theory should produce solutions that are neither acidic or basic. This is not the case. If equal amounts of HCl and ammonia react, the solution is slightly acidic. If equal amounts of acetic acid and sodium hydroxide are reacted, the resulting solution is basic. Arrhenius had no explanation for this. 3) The need for hydroxide as the base led Arrhenius to propose the formula NH4 OH as the formula for ammonia in water. This led to the misconception that NH4OH is the actual base, not NH3. In fact, by 1896, several years before Arrhenius announced his theory, it had been recognized that characteristic base properties where just as evident in such solvents as aniline, where no hydroxide ions were possible. 4) H+, a bare proton, does not exist for very long in water. The proton affinity of H2O is about 799 kJ/mol. Consequently, this reaction: H2O + H+ ---> H3O+ happens to a very great degree. The "concentration" of free protons in water has been estimated to be 10Â¯130 M. A rather preposterous value, indeed. The Arrhenius theory of acids and bases will be fully supplanted by the theory proposed independently by Johannes BrÃ¸nsted and Thomas Lowry in 1923.

About the Author