

THE STRUCTURE OF WATER IN AQUEOUS SOLUTIONS.

BY D. D. ELEY.

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1. Introduction.—Earlier papers in this series have attempted to interpret the thermodynamic data associated with the solution of gases or gas ions in solvents^{1, 2, 3, 4}. They dealt with the properties of solutions at high dilution, where the interaction between the solute particles may be neglected. The general approach has been to calculate the energy and entropy of solution of the gas molecule, starting from a simple model of the solution process. The essence of the calculation has involved an estimate of the solute-solvent interaction, utilising a knowledge of the forces involved, such as Van der Waal's forces and ion-dipole forces, and in some instances it has been necessary to employ thermodynamic methods, besides the methods of statistical mechanics. Where a statistical treatment based upon a more or less clear-cut model must be supplemented by the thermodynamic methods, the result can only be regarded as an exploration, to be substituted in time by a full statistical treatment. The combination of methods has, however, served its purpose as an essential preliminary analysis, and has furnished an "explanation," though not a proper molecular picture, of the main data on the solution of gases in solvents.

This paper has a limited objective, dealing separately with three specific points which eventually should be susceptible to a unified treatment. The nature of these points, and their significance to the general problem, is outlined in the following paragraphs.

In any calculation of the energy of solution of a gas, or hypothetical gas, in a solvent we are concerned essentially to calculate the sum of a negative solute-solvent interaction energy term and a positive cohesive energy term for the solvent. For the case of gas-ions in water the solute-solvent term is a relatively enormous term, compared to the cohesive term, and a straightforward calculation gives values of the energy of solution in good agreement with experiment.⁵ A development of this

¹ Eley and Evans, *Trans. Faraday Soc.*, 1938, **34**, 1093 (Ions in Water).

² Eley, *ibid.*, 1939, **35**, 1281 (Gases in Water).

³ *Ibid.*, 1421 (Gases in Water and Organic Solvents).

⁴ Eley and Pepper, *ibid.*, 1941, **37**, 581 (Ions in Methyl Alcohol).

⁵ Bernal and Fowler, *J. Chem. Physics*, 1933, **1**, 515.

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