of the tetraalkylammonium ions and the depressing effect[36] of the tetraalkylammonium ions on the temperature of maximum density of water.

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36) A. J. Darnell and J. Greyson, *J. Phys. Chem.* **72**, 302 (1968)

THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 43, NO. 2, 1973

"VOID" AND "EXPANSION" VOLUME CONTRIBUTIONS TO REACTION AND ACTIVATION VOLUMES OF NEARLY NONPOLAR REACTIONS

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The reaction volume, ΔV, (and the activation volume, $\Delta V^{\neq}$) of nearly nonpolar reactions are divided into three terms: i) van der Waals volume change, ΔV_W, ii) void volume change, ΔV_V and iii) expansion volume change, ΔV_E. Each contribution is estimated by means of Bondi's V_W, Miller's V_0 (volume of the hypothetical liquid at 0°K) and the known densities of hydrocarbons for the reactions of pure liquids. Unexpectedly the results clearly indicate that ΔV_W is a rather minor factor.

Introduction

There is one well-known but very often overlooked fact about liquid, *i. e.*, about one half of the volume is empty. It is easily forgotten especially when we use bulk properties, for instance, dielectric constant. Although the continuum model of solvent is quite often successful[1], it fails also quite often to reproduce the observed phenomena probably because of its basically wrong description of liquids. In this communication, we would like to demonstrate that the discontinuity of liquid is one of the essential factors that must be taken into account in the interpretation of reaction volumes and activation volumes for nearly nonpolar reactions on the basis of the known volume properties of liquids.

Discussion

Nomenclature

Because of the current confusion of the terminology, it is necessary to make the definitions of several terms clear before we start discussion[2]. The following definitions and symbols are adopted in this communication.

(*Received September 25, 1973*)

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1) For example, see E. S. Amis, "Solvent Effects on Reaction Rates and Mechanisms", Academic Press, New York (1966)
2) J. H. Hildebrand, J. M. Prausnitz and R. L. Scott, "Regular and Related Solutions", p. 42, van Nostrand Reinhold, New York (1970)