

Activation and reaction volumes and their correlations with the entropy and enthalpy parameters

Kornilov D., Kiselev V.

Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

© 2015 American Chemical Society. Data for the enthalpies, entropies, and volumes of 271 liquid compounds at standard conditions as well as those for 103 isomerization and decomposition reactions have been collected and compared. It was observed that the values of liquid molar volumes are proportional to the standard molar entropies of these compounds ($R = 0.9378$, $N = 271$). For the reactions under consideration, the proportionality ΔV_{r-n} vs ΔS_{r-n} ($R = 0.9019$, $N = 103$) was also found. The correlation between the volume and enthalpy changes in these reactions, ΔV_{r-n} vs ΔH_{r-n} , was not established ($R = 0.5719$, $N = 103$). The angular coefficient values, namely, 3.8 (eq 7) and 3.8 (eq 11), are close to the value 4.4 (eq 3), observed for the dissociation of acids and bases. The proportionality between the changes of the volume and entropy of activation (ΔV^\ddagger vs ΔS^\ddagger) at normal and elevated pressure has been also noted, whereas proportionality with the enthalpy of activation (ΔV^\ddagger vs ΔH^\ddagger) under these conditions was not observed.

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