Affinity and Reaction Rates: Reconsideration of Theoretical Background and Modelling Results

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The phenomenological affinity approach to chemical kinetics based on mass-action rate expression is revised. It is shown that the reaction rate is not an unambiguous function of affinity and that in ideal mixtures with only elementary reactions thermodynamic coupling, i. e. a positive reaction rate and negative affinity of some reaction step at the same time, is not possible. Neither does thermodynamic coupling occur in a non-ideal system of elementary reactions where the mass-action rate equation is written with activities in place of concentrations. The non-ideality and/or non-equality of reaction orders to stoichiometric coefficients lead to more complex affinity-rate relationships than commonly given which puts no explicit restrictions on affinity and rate signs. Theoretical considerations are completed with results of numerical modelling made on several simple mechanisms. Various combinations of affinity and rate signs and complex affinity-rate profiles were obtained. Modelling results support the idea that affinity is much more a result of the time evolution of a reacting system and corresponding time profiles of concentrations than the actual cause of reaction rates.

Key words: Affinity; Chemical Kinetics; Reaction Rate.