

## Ritchie equation

The *linear free-energy relation*:

$$\log k_{\text{N}} = \log k_0 + N_+$$

applied to the reactions between nucleophiles and certain large and relatively stable organic cations, e.g. arenediazonium, triarylmethyl and aryltropylium cations in various solvents.  $k_{\text{N}}$  is the rate constant for reaction of a given cation with a given nucleophilic system (i.e. given nucleophile in a given solvent).  $k_0$  is the rate constant for the same cation with water in water, and  $N_+$  is a parameter which is characteristic of the nucleophilic system and independent of the cation. A surprising feature of the equation is the absence of a coefficient of  $N_+$ , characteristic of the substrate (*cf.* the  $s$  in the *Swain–Scott equation*), even though values of  $N_+$  vary over 13 log units. The equation thus involves a gigantic breakdown of the *reactivity–selectivity principle*. The equation has been extended both in form and in range of application.

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