

linear free-energy relation

A linear correlation between the logarithm of a rate constant or equilibrium constant for one series of reactions and the logarithm of the rate constant or equilibrium constant for a related series of reactions. Typical examples of such relations (also known as linear Gibbs energy relations) are the *Brønsted relation*, and the *Hammett equation* (see also *σ -constant*).

The name arises because the logarithm of an equilibrium constant (at constant temperature and pressure) is proportional to a standard free energy (Gibbs energy) change, and the logarithm of a rate constant is a linear function of the free energy (Gibbs energy) of activation.

It has been suggested that this name should be replaced by linear Gibbs energy relation, but at present there is little sign of acceptance of this change.

The area of physical organic chemistry which deals with such relations is commonly referred to as 'Linear Free-Energy Relationships'.

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