Hammond principle (Hammond postulate)
The hypothesis that, when a *transition state* leading to an unstable *reaction intermediate* (or product) has nearly the same energy as that intermediate, the two are interconverted with only a small reorganization of molecular structure. Essentially the same idea is sometimes referred to as 'Leffler's assumption', namely, that the transition state bears the greater resemblance to the less stable species (reactant or reaction intermediate/product). Many text books and physical organic chemists, however, express the idea in Leffler's form, but attribute it to Hammond.
As a corollary, it follows that a factor stabilizing a reaction intermediate will also stabilize the transition state leading to that intermediate.
The acronym 'Bemahapothle' (Bell, Marcus, Hammond, Polanyi, Thornton, Leffler) is sometimes used in recognition of the principal contributors towards expansion of the original idea of the Hammond postulate.
See also *More O'Ferrall–Jencks diagram.*
1994, *66,* 1119